DURABILITY ASSESSMENT OF MULTIWALLED CARBON-NANOTUBES MODIFIED ADVANCED FIBROUS POLYMERIC COMPOSITE IN DIFFERENT MARINE ENVIRONMENT

A thesis submitted to

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
In Partial Fulfilment of the Requirements for the Degree of Bachelor of Technology

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National Institute of Technology
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CERTIFICATE

This is to certify that the thesis entitled, **'Durability assessment of carbon nano tubes modified advanced fibrous polymeric composite in different marine environment'** submitted by **Abhisek Agrawalla (111MM0264)** and **Namrata Keshri (111MM0365)** in partial fulfilment of the requirements for the award of Bachelor of Technology Degree in Metallurgical & Materials Engineering at the National Institute Of Technology, Rourkela, is a bonafide and authentic research work carried out by them under our supervision and guidance over the last one year (2014-15).

To the best of our knowledge, the work embodied in this thesis has not been submitted earlier, in part or full, to any other university or institution for the award of any Degree or Diploma.

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"A teacher can teach a student a lesson for a day if he could teach practically; he would remember the learning process throughout his life".

The knowledge we gained and skill acquired during the whole course of the project working at the laboratory, Metallurgical and Materials Engineering Department, will stay with us for a long time.

We would like to convey our heartfelt gratitude and regards to our project supervisors **Prof. B.C. Ray and Prof. Rajesh Kumar Prusty**, Department of Metallurgical & Materials Engineering, National Institute of Technology, Rourkela for his outstanding guidance and for giving us such a mind stimulating and innovative project. He has always bestowed parental care upon us and evinced keen interest in solving our problems. An erudite teacher, a magnificent personality and a strict disciplinarian, we consider ourselves fortunate to have worked under his supervision.

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Date: — Place:

List of Symbols

F Rate of transfer of water molecules per unit area of cross-section of the material (kg/m^2s)

D Diffusion coefficient or diffusivity of the moisture in the material (m^2/s)

C Moisture concentration in the material (kg/m^3)

l Height of the material (mm)

w Width of the material (mm)

h Thickness of the material (mm)

t Exposure time (s)

M Percentage moisture content in the material

k Boltzmann's constant ($1.38 * 10^{-23}$ J/K)

n Number density of mobile water molecules ($molecules/cm^3$)

μ Dimensionless hindrance coefficient

β Probability per unit time that a bound water molecule becomes mobile ($days^{-1}$)

γ Probability per unit time that a mobile water molecule becomes bound ($days^{-1}$)

κ Characteristic diffusion constant

I Positive odd integer

Subscripts x, y, z in x, y and z directions

t at time t

∞ at saturation level

Abstract:

Fibre reinforced polymer (FRP) composite is one of the most promising material system of 21st century due to high strength to weight ratio, non-corrosive nature, flexibility and easy fabrication. FRP has enormous demand for application in diversified fields like aerospace, submarines, underwater pipeline, automobiles, architectural components, satellites etc. Major dilemma is faced by researchers, when FRP composites are exposed to harsh and hostile environments. FRP composites are prone to degradation when exposed to humid environments, cryogenic environments, high temperature, different radiation environments such as UV and microwave, thermal spikes and shocks etc. Due to this, environmental degradation of FRP composite is a progressing area of research.

The current experiment deals with *'*Durability assessment of carbon nano tubes (CNT) modified advanced fibrous polymeric composite in different marine environment*'*. The material system used were GFRP, GFRP+0.1wt.%CNT, GFRP+0.3wt.%CNT and GFRP+0.5wt.% CNT, which were exposed to different environmental conditions , 35°C water, 5°C water and hygrothermal conditioning. All the samples showed decrease in properties when exposed to moisture due to plasticization, but the degradation shown by GFRP+0.1%CNT was the least due to minimum absorption of water in the first two environmental conditioning and showed the best mechanical properties due to uniform dispersion and higher surface area.

Hence, nano filler modification should be done judiciously to derive the best properties from FRP composites. If more wt % of CNT is used then it would result in agglomeration, formation of voids and provide sites for micro crack nucleation which will ultimately result in failure of composite.

Keywords: FRP, Carbon nano tube, Fick's diffusion, flexural strength, delamination, moisture absorption, riverline markings and CNT bridging.

TABLE OF CONTENTS:

1) INTRODUCTION

1.1) COMPOSITES:

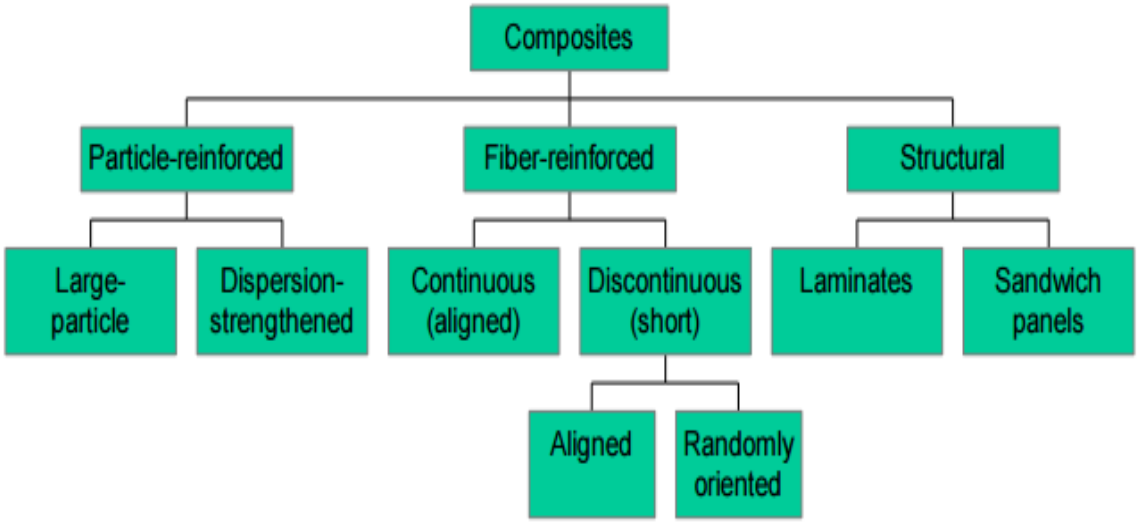
Composite materials are judicious combination of two or materials that results in improved properties than those of the individual components used alone. In contrast to metallic alloys, each component retains its separate physical, chemical and mechanical properties.

The two main constituents of composite are:

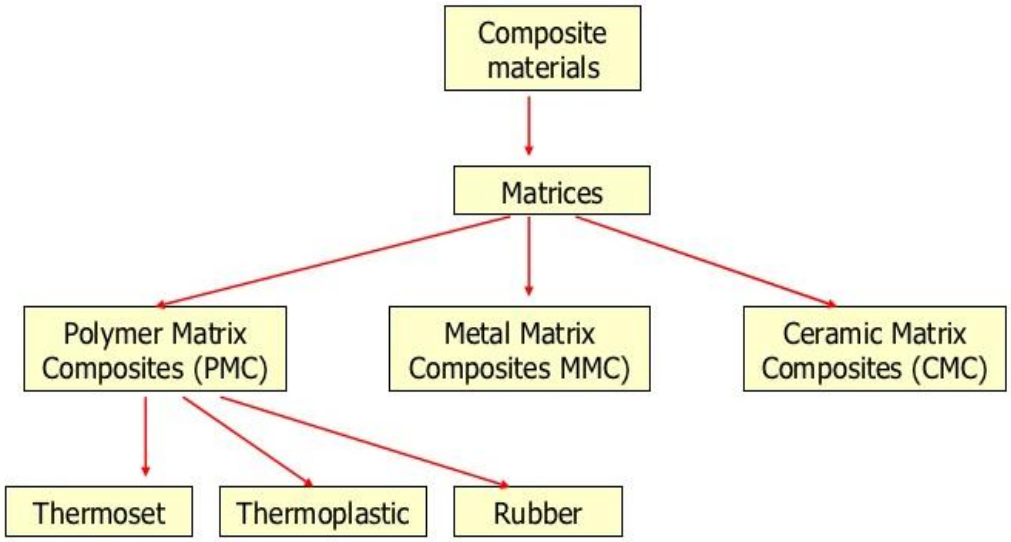
i. Reinforcement
ii. Matrix

Classification of Composites:

- Based on reinforcements :



❖ Based on matrix:



1.1.1) Matrix:

Matrix is a continuous phase and surrounds the other phase. In general, metals and polymers are used as matrix materials because some ductility is desirable.

Matrix phase serves several functions:

i. It binds the fibres together and holding them aligned in the applied stresses directions. Loads applied to the composites are then transferred to the fibres.
ii. It must isolate the fibres from each other so that they can act as separate entities.
iii. It should prevent the mechanical damage and environmental attack of fibres filaments.
iv. A ductile matrix improves fracture toughness of composite by providing means of slowing down cracks.

Polymer matrix:

Polymers are the most commonly used as matrix in composites. Structure of polymers are very complex. Polymers have low strength, low modulus and lower use temperature limits, poor thermal and electrical conductivity because of covalent bonding and are also susceptible to ultraviolet radiation, moisture and some solvents. Polymers, however, are cheap, can be easily processed and are resistant to chemical attack.

There are two major types of polymers based on their behaviour used as composite matrices- thermosets and thermoplastics.

Thermosets and thermoplastics:

Thermosets undergo a curing reaction that involves cross-linking of polymeric chains. Due to this cross-linking density, chains are less mobile and thus results in strong and rigid polymers. The curing takes place on adding chemical reagents or by applying pressure or heat.Common examples of thermosets include epoxy, polyester, vinyl ester, phenolic.

Thermoplastics are polymers that soften or melt on heating and harden when cool to room temperature. They are characterised by random arrangement of chains and amorphous structure and do not involves any cross-linking of chains. Examples of thermoplastic polymers are polyethylene, PMMA, high and low density polystyrene.

1.1.2) Reinforcements:

Fibres:

Fibres are used in the composites because of their high strength and high stiffness. Fibres are classified into long or continuous fibres and short or randomly oriented. Mostly used advanced fibres like glass, carbon, Kevlar, aramid fibres because of their high strength – weight ratio. Natural fibres like jute, cotton etc. can also be used to reinforce the composites due to their low cost. For effective use of fibres in high performance engineering materials fibres must have high aspect ratio (l/d) for achieving large fraction of load transferred to fibres, small diameter to reach high degree of flexibility and higher theoretical strength to use various techniques for making composites.

Glass fibres:

Glass fibres are the mostly used fibres as reinforcements in composites. Common glass fibres contain silica (50-60% SiO_2) and also other oxides of calcium, aluminium, sodium, boron and iron.

Types of glass fibres:

Letter designation	**Property or characteristic**
E, Electrical	Low electrical conductivity
S, strength	High strength
C, chemical	High chemical durability
M, modulus	High stiffness
A, alkali	High alkali or soda lime glass
D, dielectric	Low dielectric constant

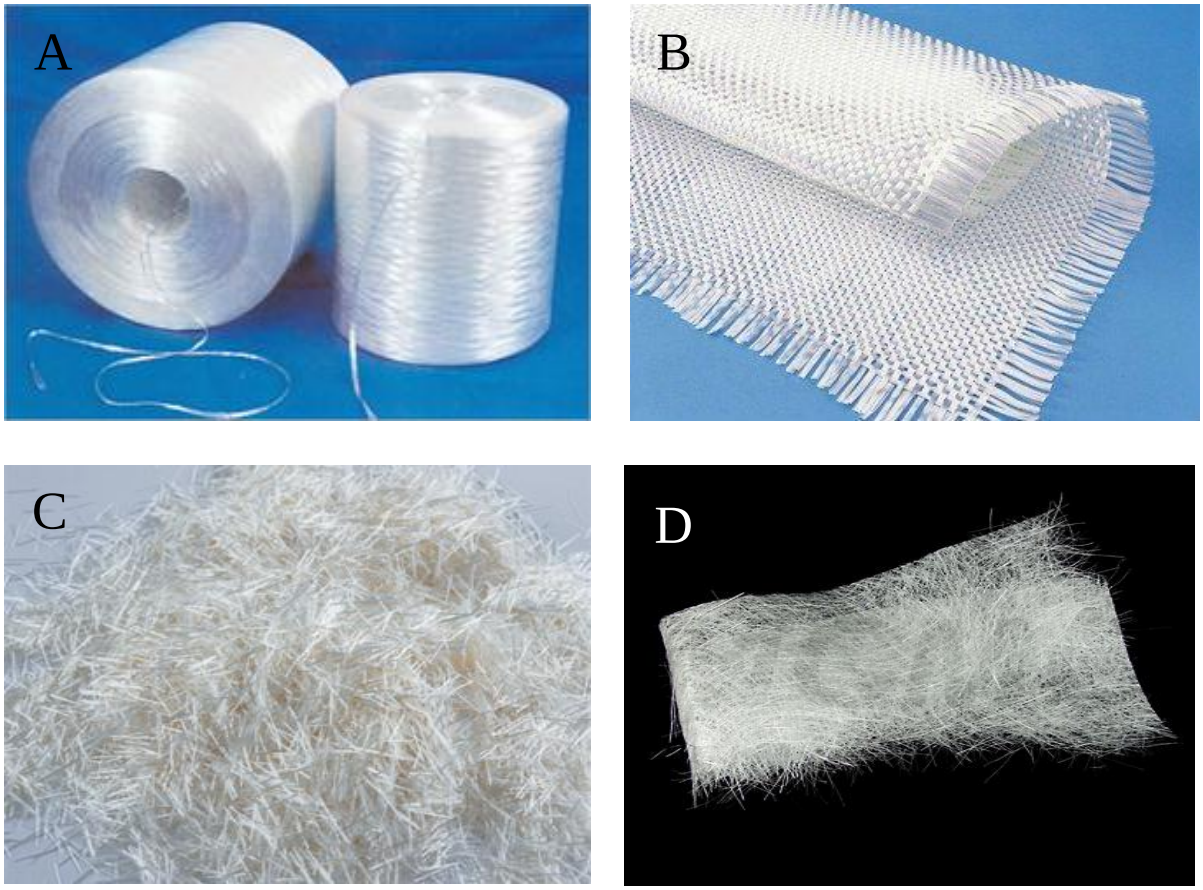


Fig 1: Common forms of glass fibres (A) continuous strands roving (B) woven roving (C) chopped fibres (D) chopped fibres mat

Carbon fibres:

Carbon can be found in a variety of crystalline form. Graphitic form of carbon is highly anisotropic with high modulus in the layer plane and very low modulus in c-direction. It is a very light weight and exhibits high tensile strength-weight ratio as well as tensile modulus-weight ratios, very low coefficient of thermal expansion, high fatigue strengths and high thermal conductivity but low strain to failure.

Property	Carbon Fibers		Carbon Nanotubes
	T300 PAN based	P120 Pitch Based	
Diameter (μm)	7	10	0.05
Density (g/cc)	1.76	2.17	~2.0
Elastic Modulus (GPa)	231	827	1000-1400
Ultimate Tensile Strength (GPa)	3.75	2.41	7-10
Thermal Conductivity (W/mK)	8	640	>2000
Coefficient of Thermal Expansion, CTE (ppm/K)	-0.6	-1.45	-1 (isotropic)
Electrical Resistivity (micro-ohm-m)	18	2.2	<0.1

1.2) Nanofillers:

Fillers are used to produce high performance polymer materials to polymer matrix composites. Pseudo one-dimensional fibres such as aluminium, glass, boron, silicon carbide, and carbon nano-fibres (CNF) have also been used over the years as fillers in composites. The introduction of MWCNT and SWCNT in composites brought about a new influx of research in lightweight high-performance reinforced polymers. Due to the unique integration of properties, CNT is used in polymer composites not only to improve strength and modulus but also to enhance the chemical resistance, thermal conductivity, electrical conductivity, and dimensional stability. It is acknowledged that the mechanical properties of the composites are significantly influenced by interfacial interactions between nanotubes and polymer matrices due to its high specific surface area. CNTs have high tendency to agglomerate due to high specific surface area, which reduces the strength of nano composites by stress concentration effect. Thus, for maintaining the strength and fracture toughness fibre volume fracture should be kept below a certain value.

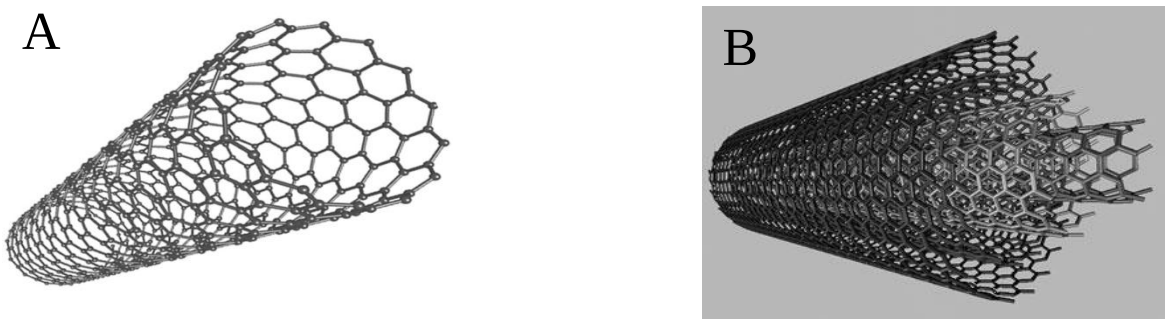


Fig 2: (A) Single walled carbon nano tube (B) Double walled carbon nano tube

1.3) Interfaces:

The bounding surface exists between reinforcement and a matrix across which a discontinuity in some properties are seen. An interface is the boundary which alters the material parameters from one side to another. For achieving good interfacial bonding between matrix and reinforcements, several factors are to be considered such as load transfer across the interface and wetting of fibre by matrix etc.

Fibre-reinforced polymer composites:

FRP composites are composites which contain fibres as reinforcements in a thermosetting polymer resin matrix.

Promising properties exhibited by FRP composites:

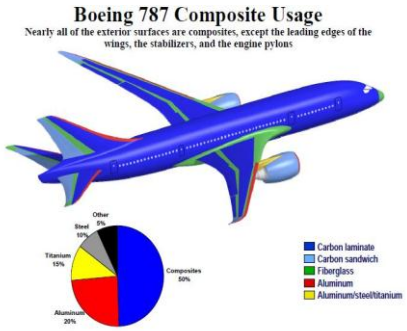
- High strength to weight ratio
- High modulus to weight ratio
- Excellent fatigue damage tolerance
- Design flexibility
- Low coefficient of thermal expansion
- High thermal conductivity- weight ratio
- High internal damping
- Non corroding behaviour

1.4) Applications of FRP Composite Materials:

Composites can be found in every fields and in day-to-day life. Several examples of natural composites are muscles, bones, wings of birds, leaves etc. Some of the commercial and industrial applications of composites are given below:

- **Aircraft/military**

  Aerospace aircrafts and their parts



- **Automobiles/transportation**

  Automobile parts and accessories

- **Structural /infrastructure**

  Cladding, building bridges and architectural structures

Figure 1: FRP is already frequently used in construction for secondary structures such as cladding, as demonstrated at this superstore in Bristol, UK. (Picture courtesy of Hill(biol FRP.)

Figure 3: Conventional FRP roof weighing 14 tonnes.

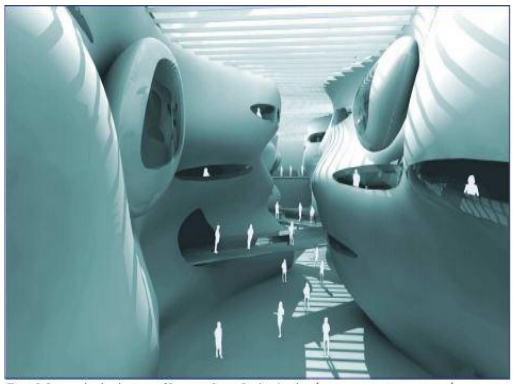


Figure 9: Proposed redevelopment of Battersea Power Station, London. (Picture courtesy of Future Systems.)

Figure 7: The Rest Zone FRP building within the Millennium Dome, London.

- **Marine applications**

Ships, submarines, naval boats

- **Pipelines applications**

- **Futuristic applications**

Figure 13: FRP classrooms (Future Systems).

Figure 12: FRP classrooms (Future Systems).

1.5) Limitations of FRP materials

Despite their surpassing performance, polymeric composites undergo deterioration due to environmental attacks (humid environments, cryogenic environments, high temperature, different radiation such as UV and microwave, thermal spikes and shocks). Polymer composites are most susceptible to moisture environment which results in significant decrease in strength of composite after exposure for long hours.

Fig. 3: (A) De-bonding failure of Young America boat in 1999 (B) broken wing of American

Airlines Flight 587

Composite structure failures have made the material science fraternity alarmed about the limited understanding of RP composites. The above fig shows the failure of composites structures due to de-bonding.

The main reason for failure in composite structures is delamination as predicted by practical experience and theory, due to this failure mode analysis of interfacial properties of FRP composites is critical.

2) Literature Survey:

2.1) Moisture ingression in FRP composites

2.1.1) Moisture ingression models

Researchers have developed different types of models to study the moisture ingression kinetics in polymeric composites. Understanding the moisture ingression process means to determine the percentage moisture concentration distribution throughout sections of FRP composites. Alfrey was the first to report three distinct types of diffusion processes in polymeric materials. There are three distinct types of classification based on the relative diffusion rates of penetrant molecules and relaxation of polymeric chains. The first is Fickian Diffusion in which relaxation rate is much higher than that of diffusion. Second includes Non-Fickian Diffusion in which the rate of relaxation is approximately same as rate of diffusion. The third category is related to a case in which rate of relaxation is much lower than rate of diffusion.

Some of the diffusion models in polymeric composites are given below.

2.1.1.1) Linear Fickian Diffusion Model

Fick in 1855 developed the simplest model applicable to most polymeric composite.. Fick's first law of diffusion is for isotropic medium, diffusion rate through any cross-section is directly proportional to the concentration gradient normal to it and is expressed as -

$$F = -D\frac{\partial C}{\partial x} \quad (1)$$

But, Fick's second law of diffusion is more fundamental and represented by equation (2) when D depends on moisture content

$$\frac{\partial C}{\partial t} = \frac{\partial\,(D\ \partial C)}{\partial x(\partial x)} \quad (2)$$

When D is independent of moisture content, equation (2) becomes –

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad (3)$$

The most satisfactory solution of Fick's second law:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4h^2}\right] \quad (4)$$

The above equation is simplified as:

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \quad (5)$$

Moisture desorption is given by:-

$$\frac{M_t}{M_o} = -\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4h^2}\right] \quad (6)$$

The diffusivity is enough to depict the behaviour of the FRP composite in case of Fickian behaviour. The coefficient of diffusion in this case does not depend on the concentration of penetrating molecules and is represented by:

$$D = \pi\left(\frac{h}{4M_\infty}\right)^2\left(\frac{M_1 - M_2}{\sqrt{t_1}-\sqrt{t_2}}\right)^2 \quad (7)$$

Typical linear Fickian behaviour is shown in Fig.4, which includes two parts - an initial linear region and a saturation region in which no further moisture absorption takes place. Fickian behaviour is more prominent when polymeric composites are exposed to humid environment and at lower temperatures. It is observed that many FRP composites follow Fick's law,

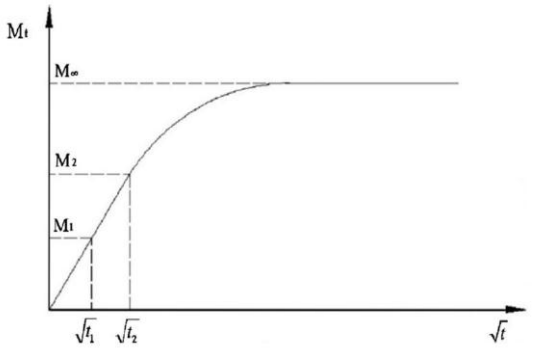
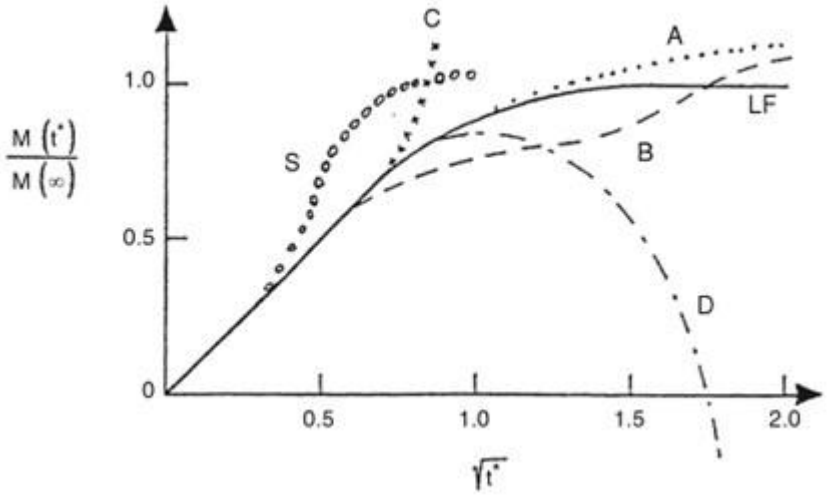


Fig. 4: Typical linear Fickian diffusion model

2.1.1.2) Deviation from Fickian Behaviour: Non-Fickian Diffusion Models

One of the most important parameter to study polymeric systems is glass transition temperature. Polymers, in glassy state deviate from Fick's law in contrast to polymers in rubbery state. Non-Fickian behaviour is because of different reasons such as development of cracks and voids, diffusion of moisture along fibre matrix interface and negligible swelling of the composites. Also, polymer matrix is important in deciding the moisture diffusion behaviour.



A–Pseudo-Fickian Diffusion

B–Dual-stage Diffusion Model

C–Rapid increase in moisture content

D–Irreversible degradation leading to weight loss

S- Sigmoidal Model

LF- Linear Fickian Model

Fig 5: Typical linear Fickian and non-Fickian diffusion models

Many researchers outlined that polymeric composites regain their original strength, even entirely or partly, on drying. In general, curves "LF", "A" and "B", are reversible on moisture absorption, original strength is completely regained, but for curves "C" and "D", permanent loss of strength was reported.

2.1.1.3) Langmuirian Diffusion Model

This model is known as the two-phase diffusion model, based on an assumption that the penetrating molecules are divided into two parts- the first part consists of the mobile molecules and hence can diffuse freely; while the other part are immobile molecules which occupy the micro-voids. There is a possibility of interchanging between both the molecules.

Langmuirian model of diffusion is a modified Fick's law, and represented as,

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \quad (9)$$

Solution for above equations is given by-

$$\frac{M_t}{M_\infty} = \frac{\beta}{\gamma+\beta} e^{-\gamma t}\left(1 - \frac{8}{\pi^2}\sum_{h=1}^{\infty(odd)} \frac{e^{-\kappa i^2 t}}{i^2}\right) + \frac{\beta}{\gamma+\beta}\left(e^{-\beta t} - e^{-\gamma t}\right) + \left(1 - e^{-\beta t}\right); 2\gamma, 2\beta \ll \kappa \quad (10)$$

For short duration of time, equation (11) can be approximated to-

$$\frac{M_t}{M_\infty} \approx \frac{4}{\pi^{3/2}}\left(\frac{\beta}{\gamma+\beta} M_\infty\right)\sqrt{\kappa t}\ ;\ 2\gamma, 2\beta \ll \kappa, t \leq 0.7\kappa \quad (11)$$

And for long duration of time, equation (10) can be modified as follows-

$$\frac{M_t}{M_\infty} \approx 1 - \frac{\gamma}{\gamma+\beta} e^{-\beta t}\ ;\ 2\gamma, 2\beta \ll \kappa, t \gg \frac{1}{\kappa} (12)$$

The two-phase diffusion model explains the kinetics of absorption of moisture in FRP composites and experimentally it is more accurate than Fick's law for certain systems.

2.1.1.4) Hindered Diffusion Model

The one-dimensional Langmuirian model is similar to one-dimensional hindered diffusion model. To incorporate the interaction between water molecules and polymeric composites and the diffusion through multiple surfaces, the three dimensional hindered diffusion model was developed.

2.1.1.5) Dual-stage Diffusion Model

Dual-stage moisture diffusion model is shown by Curve "B". The dual-stage diffusion model is divided into two parts, the polymer chain relaxation and the Fickian diffusion.

$Mt = Mt, + Mt,$ (13)

The solution to the equation (16) is given by the following equation -

$$M_t = M_{\infty,F}\left\{1 - exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right]\right\} + M_{\infty,R}[1 - exp(-kt)] (14)$$

The two-stage moisture diffusion is the combined effect of the polymer matrix relaxation and classical Fickian diffusion. The initial part of the curve is linear which is similar to the Fickian curve, that shows no influence of polymeric relaxation on it.

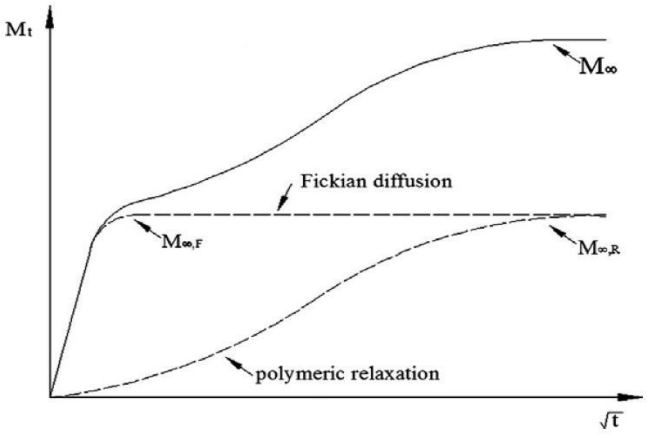


Fig. 6: Theoretical moisture ingression curves showing combined effect of polymeric relaxation and Fickian diffusion.

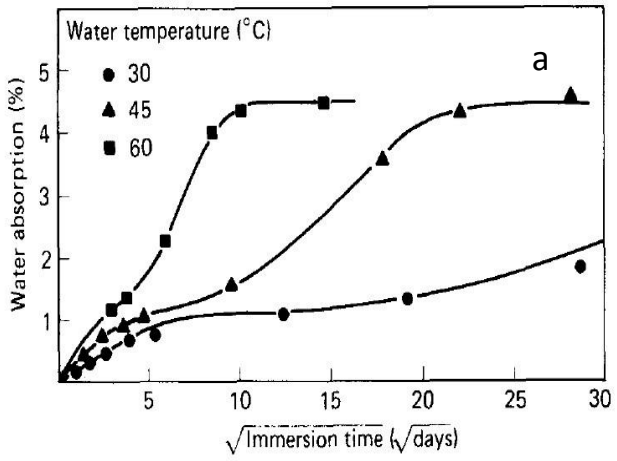


Fig. 7: Dual stage diffusion followed by polymeric composites at varying temperature.

2.1.2) Factors affecting moisture ingression kinetics in polymeric composites

2.1.2.1) Effect of Fibre system

Based on moisture absorption tendency, fibres are classified into two parts – permeable and impermeable fibres. Glass and aramid fibres are permeable, in this case moisture absorption tendency depends on both resin polymer and fibre phase. On the other hand, carbon fibres are resistant to moisture absorption and hence, moisture absorption depends only on the resin phase in carbon fibre reinforced polymer composites.

2.1.2.2) Effect of resin structure

Moisture absorption kinetics and amount of moisture absorbed depends on resin and hence, proper choice of resin system is important. Moy et.al has shown that polymer with high cross link density absorbs less moisture as compared to low cross link density. Springer showed that on modifying the catalysing agent for the same fibre/matrix system, moisture diffusion kinetics changes.

2.1.2.3) Effect of interfacial adhesion

Silane coating is provided on the glass fibres, which act as a protective coating and coupling agent to enhance the adhesion of fibre with polymer matrix. Silane is used as coupling agents to utilize chemical reactivity between the organic resin and inorganic substrate, so as to improve the adhesion at the fibre/matrix interface. Hence, it is important to create a better interphase/interface so that there is no in service failure.

2.1.3) Effect of Moisture Ingression on Mechanical Properties of FRP Composites

Polymeric composite properties are severely affected by plasticization, by inducing plastic deformation in matrix which reduces the glass transition temperature of composites. Kelley has experimentally shown that there is a reduction in glass transition temperature of nearly 20^0C for each 1% moisture absorbed.

Lassila has experimentally showed that, when exposed to water for 30 days, flexural strength of GFRP composites reduces.

2.1.4) Effect of Moisture Ingression on Failure Modes of FRP Composites

There is degradation in properties due to the degradation of fibres, the interface/interphase and/or the polymer matrix. Different irreversible and reversible physical, physico-mechanical and chemical degradation mechanisms occur as a result of different environmental conditions.

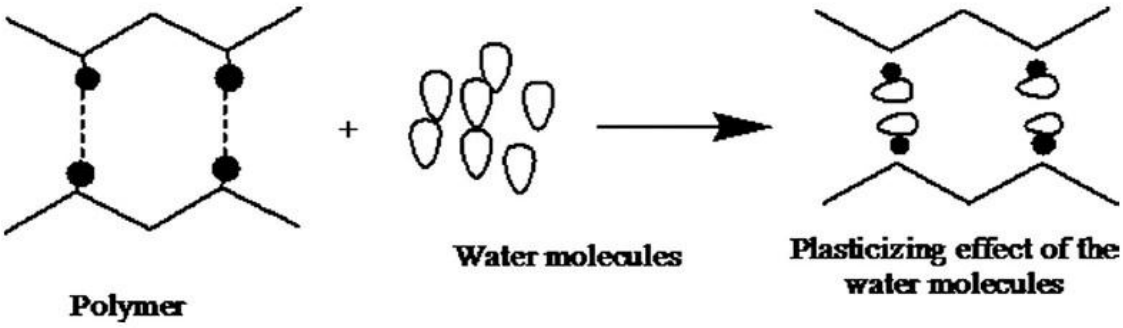


Fig. 8: Schematic diagram of plasticization caused by moisture in polymer matrix.

Physical phenomena like plasticization and swelling occurs when moisture enters the polymer matrix. Addition to this, chemical and physico-mechanical phenomena occur in

the composite such as hydrolysis and micro-void formation respectively which result in deterioration of fibres and matrix and also interface between them.

Fig. 8 shows the plasticisation process, which occurs due to interaction of water molecules with polymer chains which obstruct the existing hydrogen bonds between polymer chains and form new bonds with the polymers. It results in the swelling of the polymers due to bond-length increment between polymer chains.

Clustering of water molecules at the interface causes micro void formation in the polymer matrix and at the interface. Internal stresses are developed due to swelling caused by the absorption of moisture, leading to formation of micro voids or micro cracks.

Plasticisation and swelling are reversible in nature whereas hydrolysis, micro-cracks etc. are irreversible phenomena.

Hydrolysis is the process in which detachment of side groups from the polymer chains. In Leaching break down of the fibre/matrix interphase region occurs and resulting in separation.

3) EXPERIMENTAL:

Our experiment was focussed on three types of marine environment, firstly, exposing the sample to room temperature water (35°C), secondly, exposing the samples to cold water (5°C) and thirdly, exposing the samples to 95% relative humidity at 70°C. In the first two cases, the samples were of GFRP, GFRP+0.1 wt.% CNT, GFRP+0.3 wt.% CNT and GFRP+0.5 wt.% CNT, whereas for the third environment we chose only GFRP samples.

3.1) Materials:

Diglycidyl ether of Bisphenol A (DGEBA) type epoxy resin was used as matrix and Triethylene tetra amine (TETA) as hardener. Both were supplied by Atul Industries Ltd, India under the trade name of Lapox L-12 and K-6 respectively. The 3K plain weave glass fiber having filament diameter of 15 µm was supplied by Saint Gobain, India. It served the need for reinforcement. MWCNTs having an outer diameter of 6-9 nm and 5 µm length were supplied by Sigma-Aldrich.

3.2) Fabrication:

Before starting the hand lay-up method, in order to fabricate MWCNT fused glass/epoxy (CNT-GE) composite, the epoxy resin was modified by incorporating MWCNT to it. Matrix and fibers were approximately in 1:1 proportion by weight. The amount of CNT in CNT-GE composite was varied as 0.1 wt. %, 0.3 wt. % and 0.5 wt. % of epoxy. Three different laminates were fabricated using these different compositions. Required amount of CNT was dispersed in 150mL of acetone. This suspension was stirred for 30 minutes at 1000 rpm using magnetic stirrer. Sonication of this suspension was done for 30 minutes. The purpose of stirring and sonication is to deagglomerate the existing agglomerates of CNTs. This CNT/epoxy mixture was added to pre-weighed epoxy, which was brought to sufficient fluidity by heating. Further, stirring of epoxy/CNT/acetone mixture was done at 1000 rpm for 2 hr at 70 °C. Sonication was again carried out at 70 °C for 1 hr. At this stage, evaporation of all acetone was assured. The left epoxy/CNT suspension was vacuumed for 12 hr to facilitate removal of air bubbles entrapped in the suspension during earlier stages. Specified amount of hardener (10 wt. % of epoxy) was blended and stirred properly in the obtained suspension. The laminates were prepared by hand lay-up process using 14 layers of woven fabric E-glass fibres. Curing was done at 60 °C temperature and 10 kg/cm^2 pressure in a hot press for 20 minutes. Likewise, using the same parameters as used in CNT-GE composite, the controlled glass fibre/epoxy (GE) composite laminate was fabricated using neat epoxy and 14 layers of glass fibre by hand lay-up method followed by hot pressing. The laminates were allowed to keep at room temperature for 24 hrs. Flexural (as per ASTM D7264) samples were cut from the prepared laminates with a diamond cutter with dimensions 72 mmx12.7 mmx4 mm. The

samples were then post-cured at 140 °C for 6 hr. ILSS samples of GFRP in case of moisture environment were cut as per ASTMD2344 using diamond cutter having dimensions 32mmx8mmx4mm.

3.3) Environmental conditioning:

3.3.1) Room temperature Water (35°C)

All the samples of different composition were dipped in water. The samples were regularly weighed in initial stages of the experiment because maximum amount of moisture is absorbed within the first few hours. After 3 hours, 410 hours and 1008 hours the samples were removed and instantaneously tested at room temperature for flexural test using 3 point bending fixture of Universal Testing Machine (Instron 5967) following the ASTM D7264 standard. The loading rate was kept at 1 mm/min.

3.3.2) Cold Water (5°C)

All the samples of different were dipped in cold water placed in an ultra-low chamber. The samples were weighed in long periods of time because the absorption rate in low temperature water is very slow. After 186 hours and 720 hours the samples were removed and instantaneously tested at room temperature for flexural test using 3 point bending fixture of Universal Testing Machine (Instron 5967) following the ASTM D7264 standard. The loading rate was kept at 1 mm/min.

3.3.3) Hygrothermal Conditioning

In this we had two sets of GFRP samples. One was according to ASTM D2344 and other one according to ASTM 7264. The samples were exposed to 95% RH at 70°C in a hygrothermal chamber. It was weighed regularly to study the absorption kinetics. The samples were exposed for 1080 hours then it was removed and instantaneously tested at room temperature for flexural test and ILSS test using 3 point bending fixture of Universal Testing Machine (Instron 5967) following the ASTM D7264 and ASTM D2344 standard. The samples were tested at four different loading rates (1, 10, 100 and 1000mm/min).

4) Results and Discussions:

4.1) Effect of room temperature (35°C) water conditioning on different material systems(GFRP, GFRP-0.1%CNT, GFRP-0.3%CNT, GFRP-0.5%CNT)

4.1.1) Moisture ingression behaviour in different material systems.

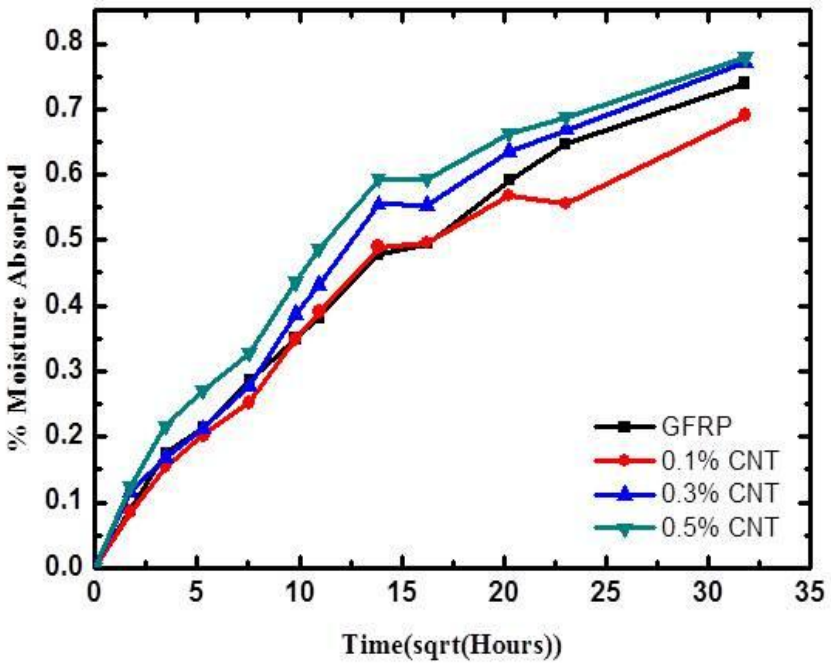
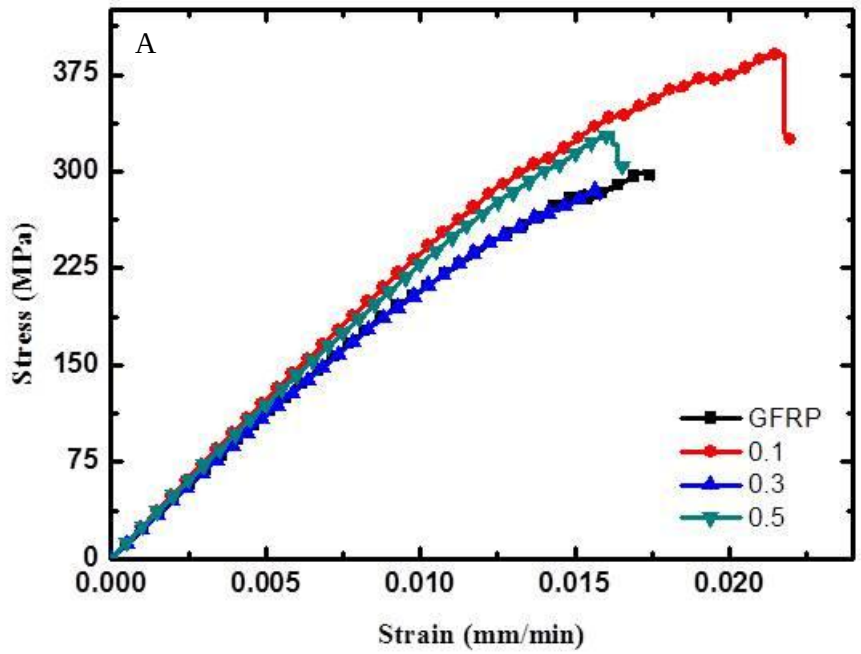


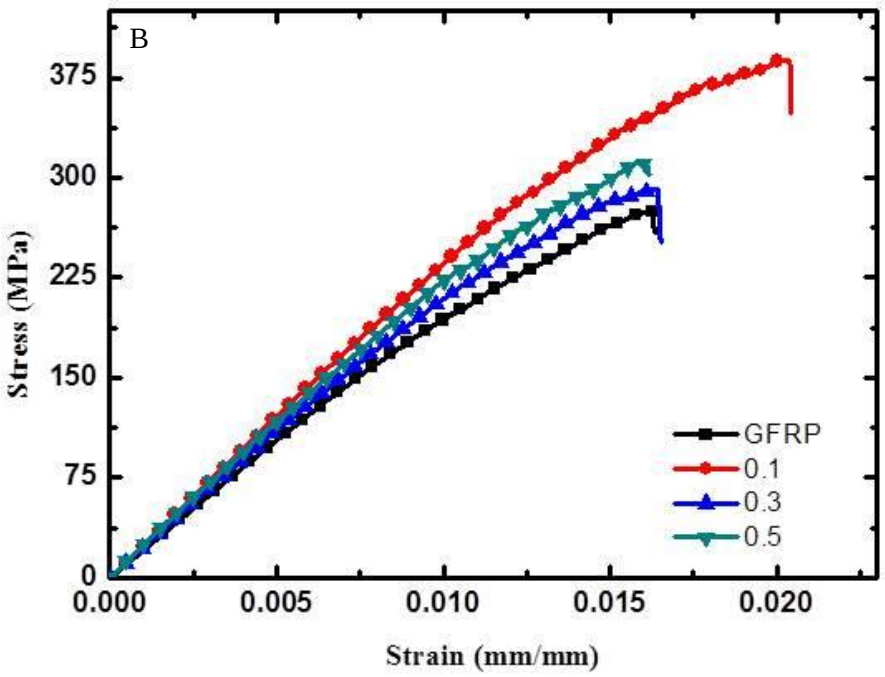
Fig 9: Moisture absorption by different materials with increasing exposure time.

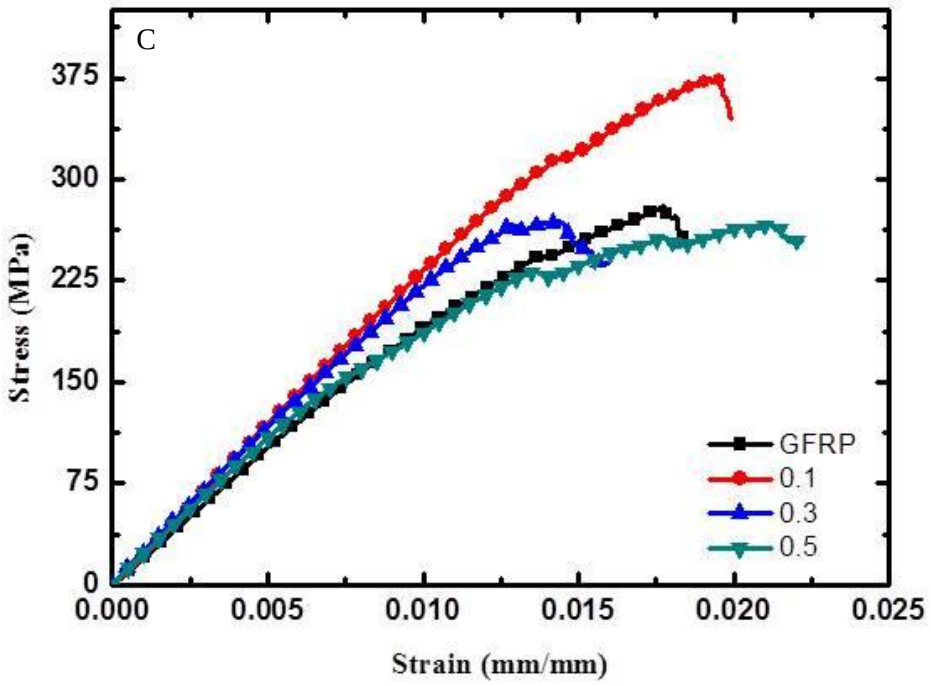
In this graph, it is observed that the moisture absorbed by GFRP-0.5%CNT is much higher than the GFRP and GFRP-0.1%CNT. This may be due to the high concentration of CNTs present in 0.5%CNT composites leading to agglomeration or formation of lumps resulting more void spaces created in the composites to accommodate water molecules.

GFRP-0.1%CNT shows least moisture uptake because of the uniform dispersion of the CNTs throughout the matrix resulting good network structure between epoxy and CNTs and reduces the void spaces which are susceptible to absorb moisture.

4.1.2) Effect of moisture absorption on mechanical properties with increasing exposure time.







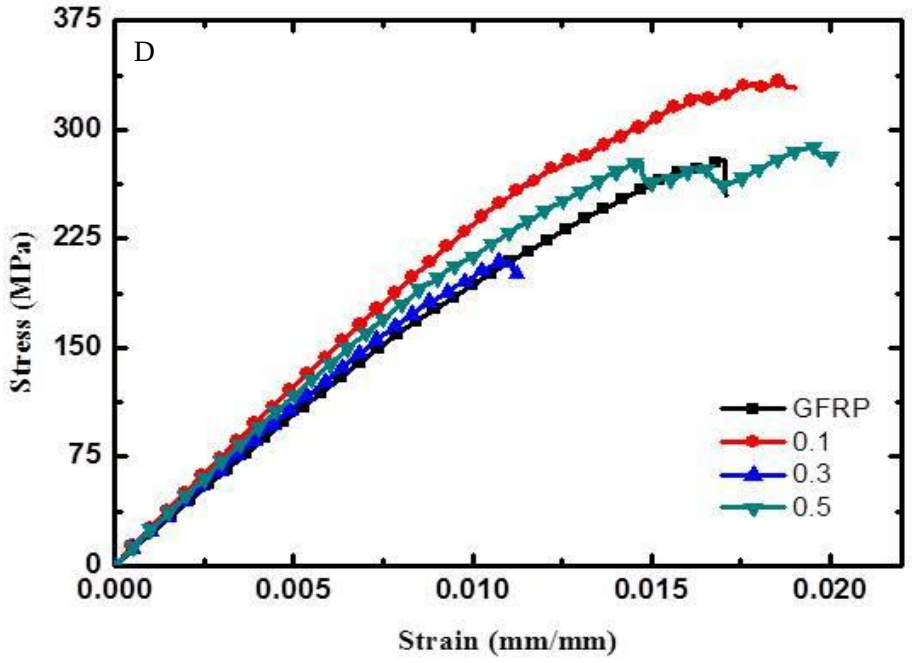
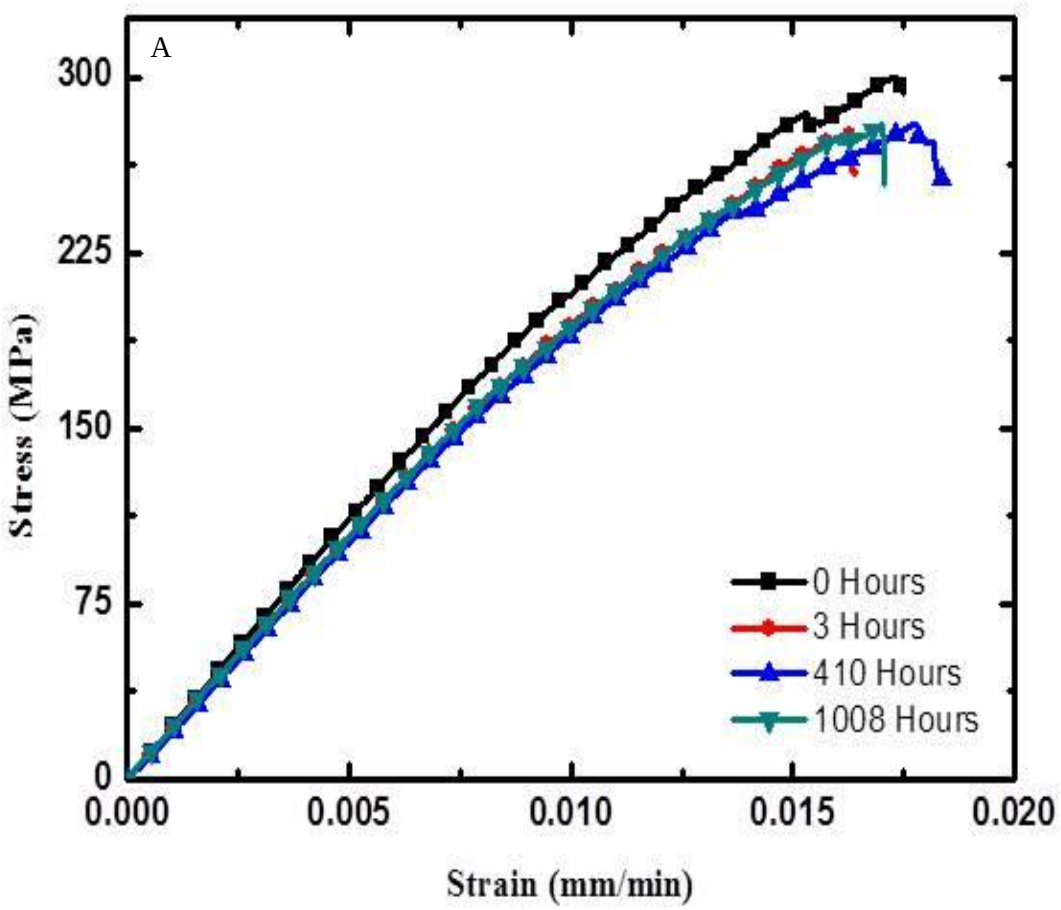
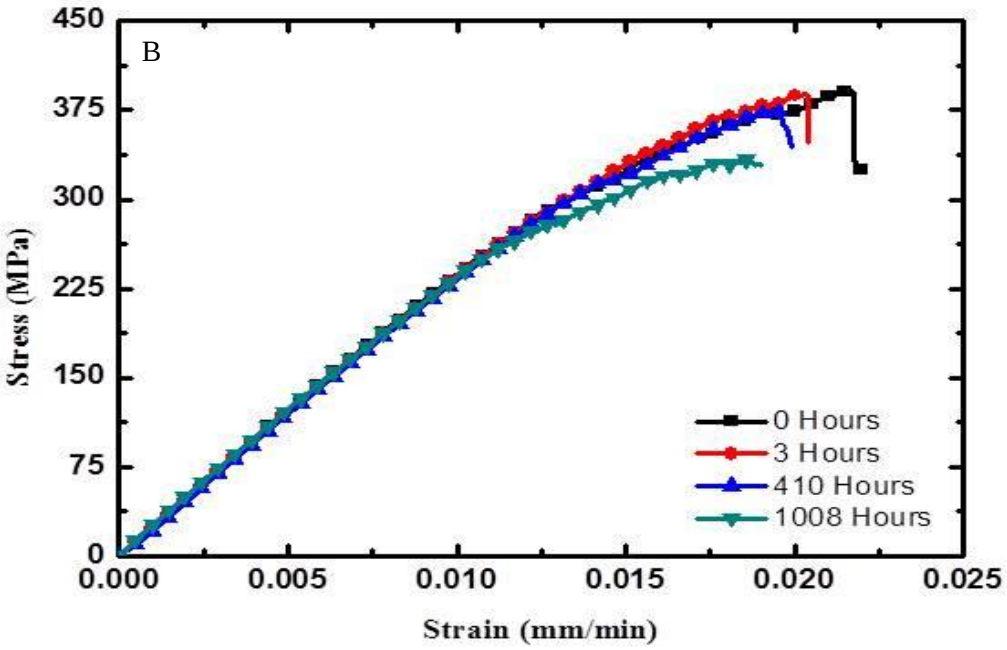


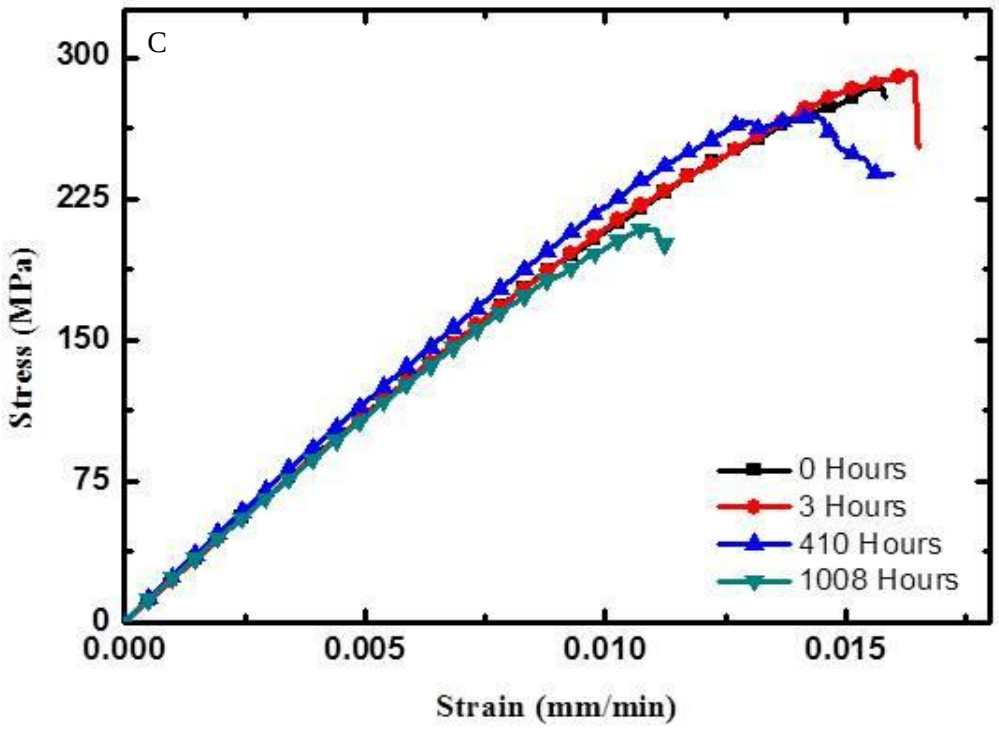
Fig 10: Stress-strain diagrams of different material systems at different exposing time in room temperature water (A) without conditioning (B) 3hours (C) 410 hours (D) 1008 hours

In case of (A), 0.1%CNT shows the highest strength at failure strain as compared to GFRP due to uniform dispersion of CNTs which provides high interfacial area responsible for better load transfer capacity to fibres. Addition of CNT shows the better properties due to its high specific surface area. After long exposure in water, significant decrease in properties can be seen in every materials due to moisture absorption leading to plasticization in the composites. But 0.1%CNT shows the better properties in comparison to other material systems.

4.1.3) Effect of exposure time on mechanical properties of individual material systems.




B
450
375
300
225
150
75
0
Stress (MPa)
0.000
0.005
0.010
0.015
0.020
0.025
Strain (mm/min)
0 Hours
3 Hours
410 Hours
1008 Hours


C
300
225
150
75
0
Stress (MPa)
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0.005
0.010
0.015
Strain (mm/min)
0 Hours
3 Hours
410 Hours
1008 Hours

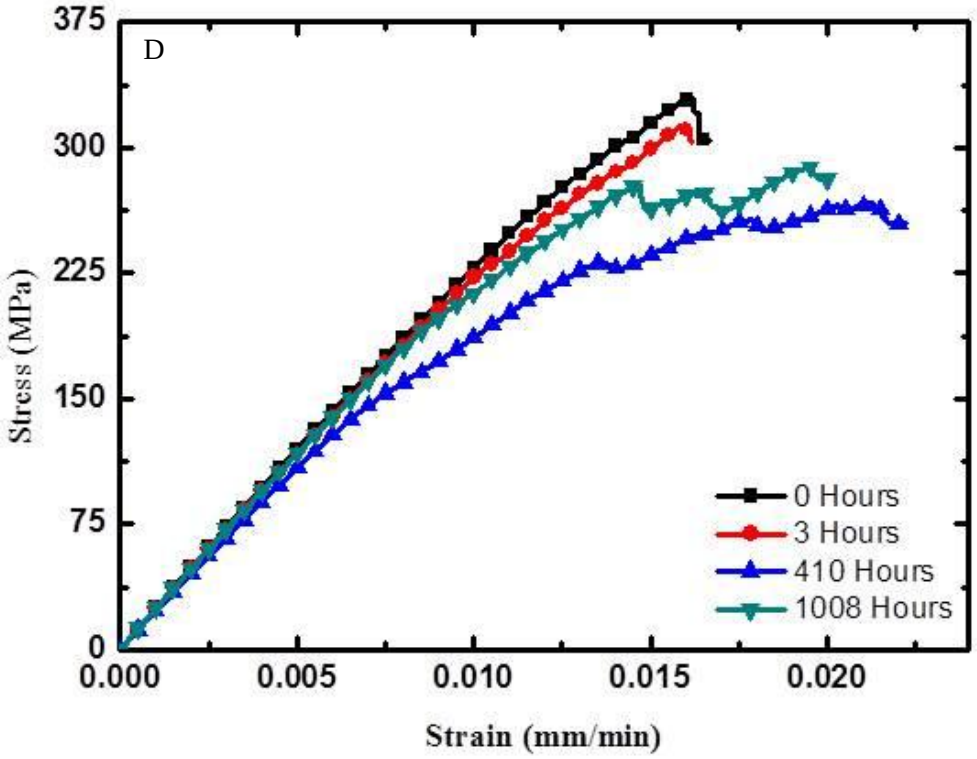
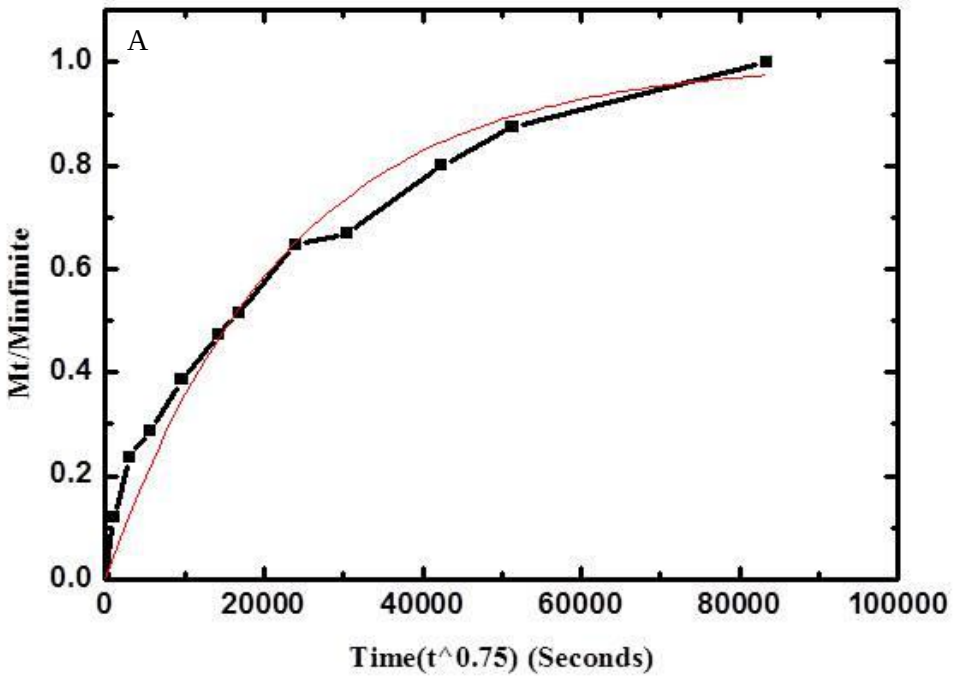
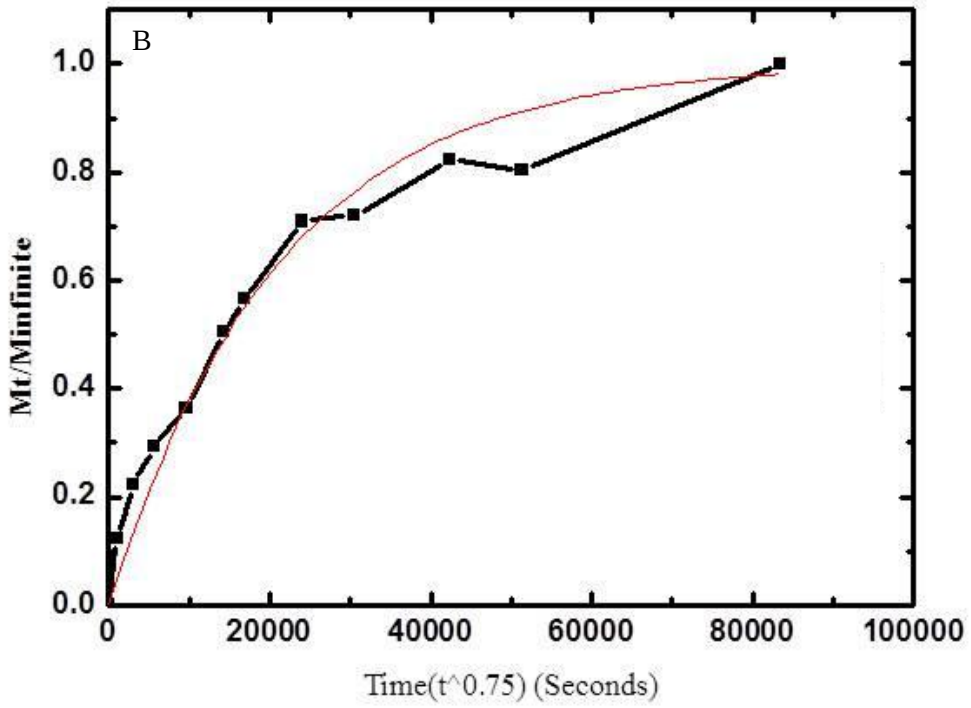


Fig. 11: Stress –strain diagrams at different exposing time in room temperature water (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

With increasing conditioning time, degradation in properties is observed in all the systems.

4.1.4) Moisture ingression kinetics of different material systems





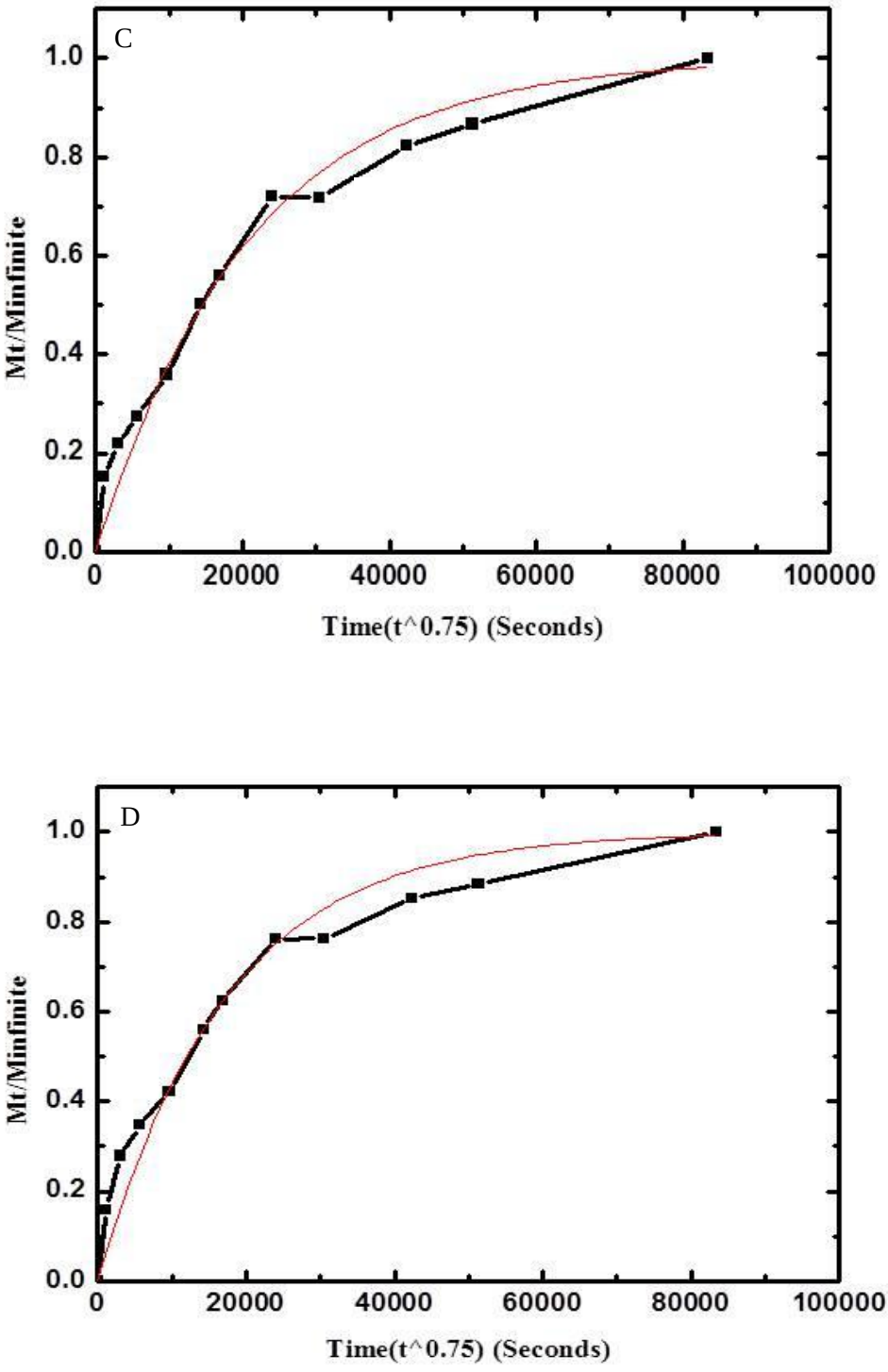
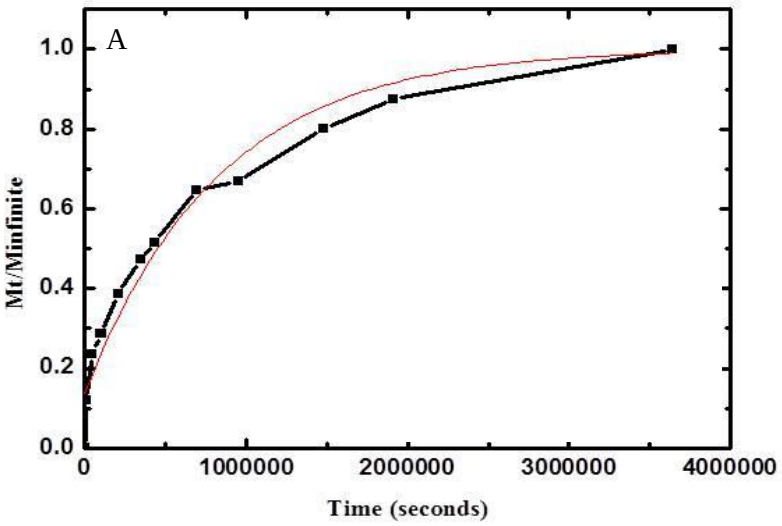
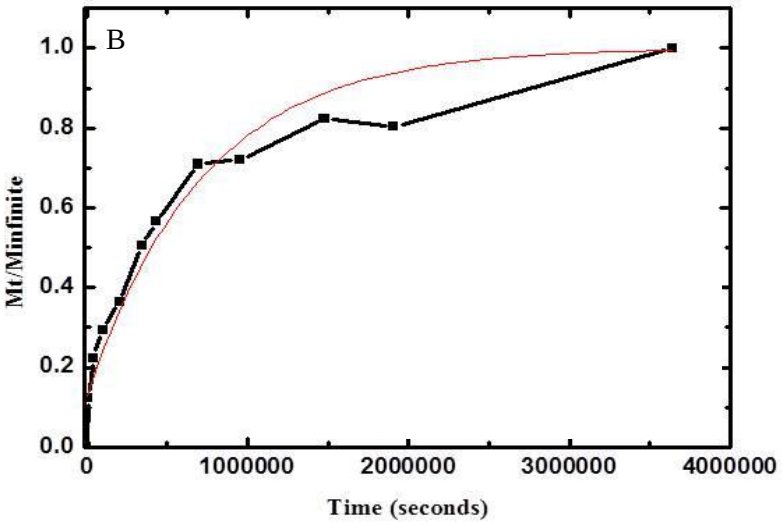


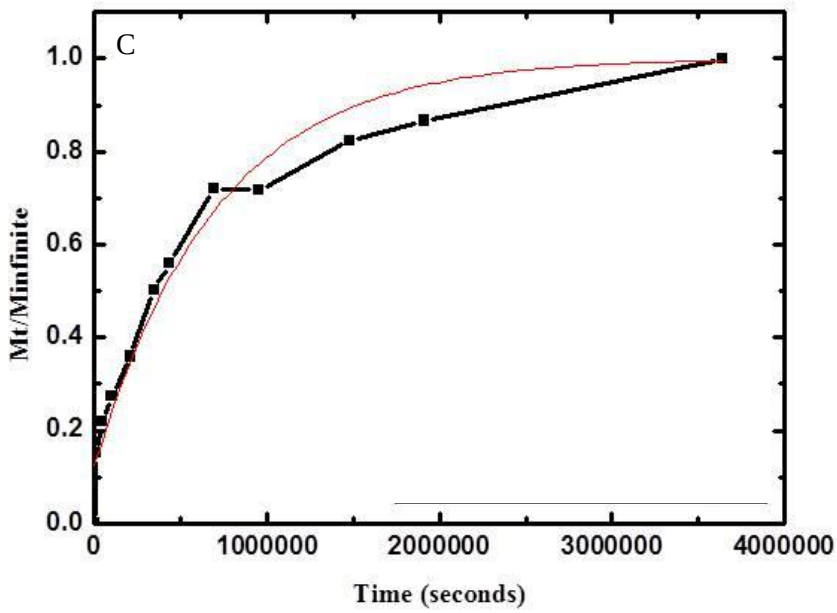
Fig. 12: Fick's Moisture diffusion fitting curves obtained (conditioned in room temperature water) (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

The moisture absorption kinetics initially follows linear curves which represents Fickian behaviour and after that it seem to follow dual-stage diffusion which can be confirmed after long exposing time. The Fickian curve is fitted using equation no. 5 in origin, and diffusivity is calculated for different systems.

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \quad (5)$$







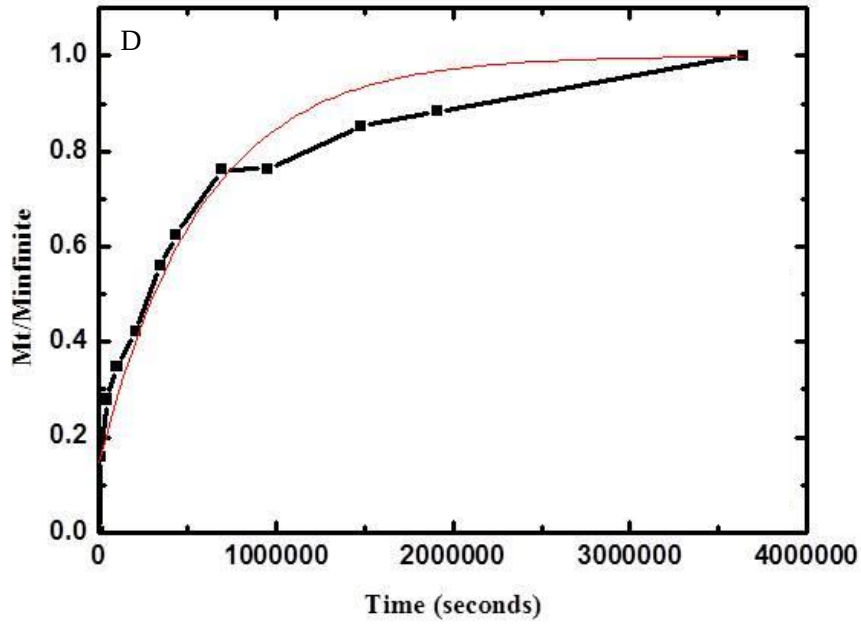


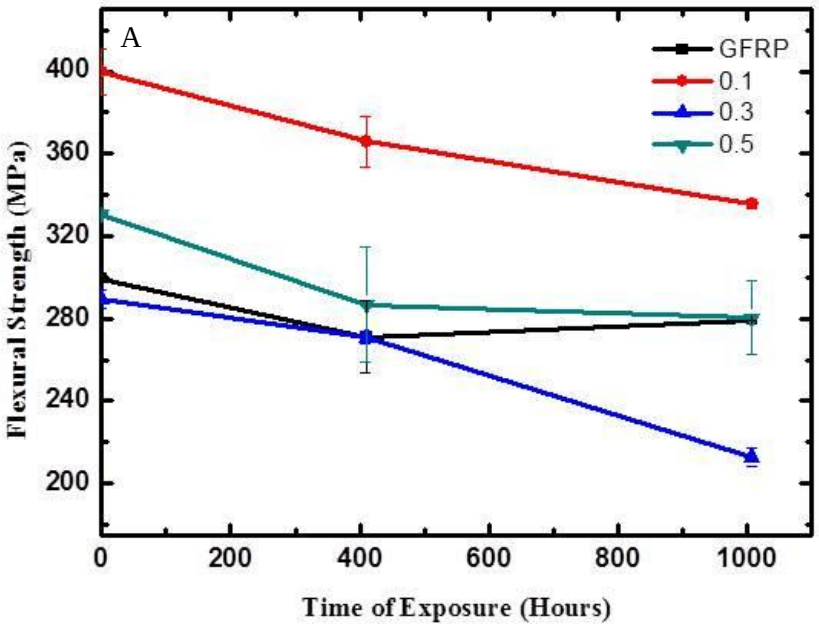
Fig. 13: Langmurian diffusion fitting curves obtained (conditioned in room temperature water) (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

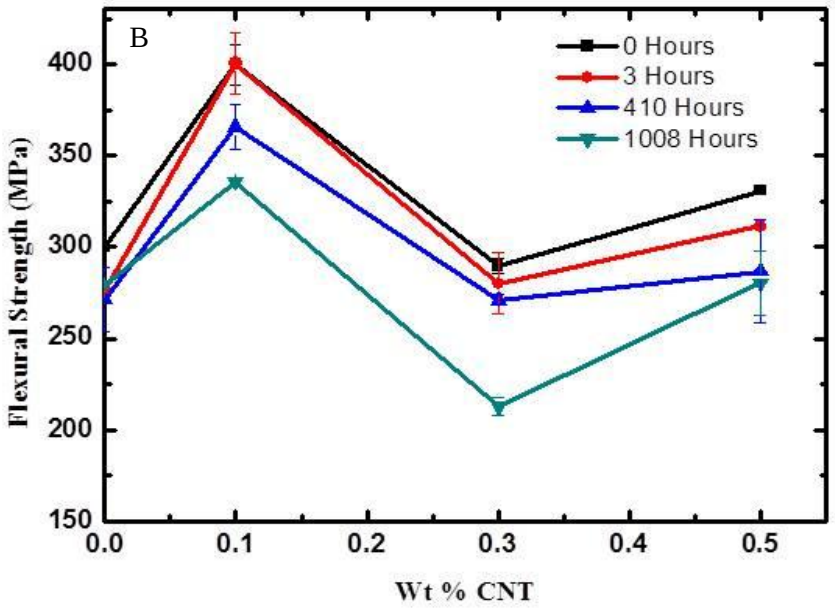
Langmurian curve is fitted in equation no. 12 using origin, and the values of alpha and gamma are calculated.

$$\frac{M_t}{M_\infty} \approx 1 - \frac{\gamma}{\gamma+\beta} e^{-\beta t} \; ; \; 2\gamma, 2\beta \ll \kappa, t \gg \frac{1}{\kappa} \quad (12)$$

It is reported by many researchers that Langmurian diffusion model is more accurate than Fick's diffusion model.

4.1.5) Effect of moisture ingression on flexural strength and flexural modulus





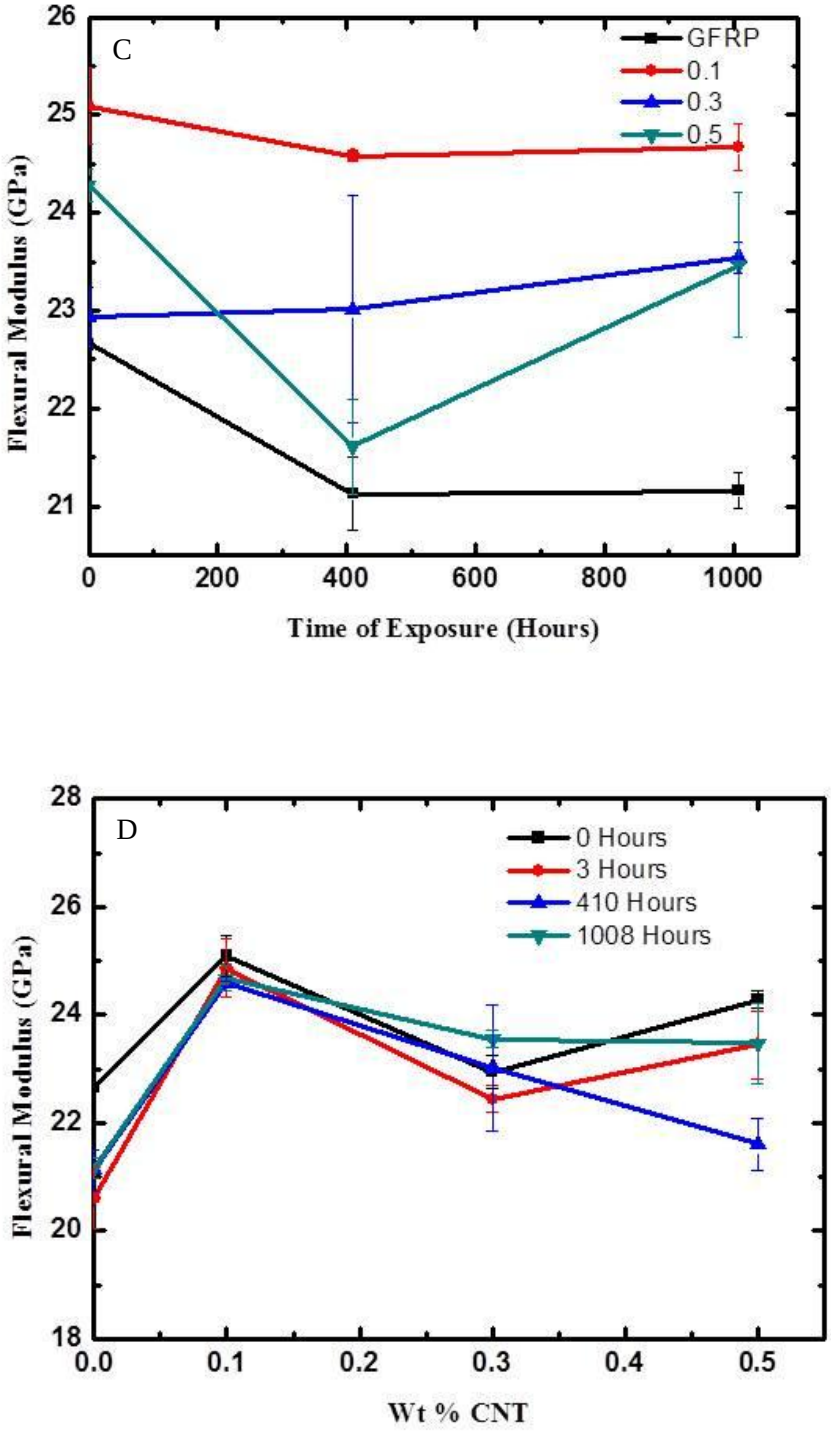


Fig. 14: At room temperature (35°C) water conditioning (A) Flexural strength vs exposure time (B) flexural strength vs wt%.CNT (C) flexural modulus vs exposure time (D) flexural modulus vs wt%.CNT

From fig.(A), it is observed that 0.1%CNT exhibits higher flexural strength as compared to others. With increasing exposing time, rate of degradation in properties is much higher in case of 0.1%CNT as well as 0.3%CNT whereas the rate of degradation in GFRP and

0.5%CNT is less as compared to others. It is also observed that flexural strength reduces with conditioning time in all the material systems due to plasticization and hydrolysis.

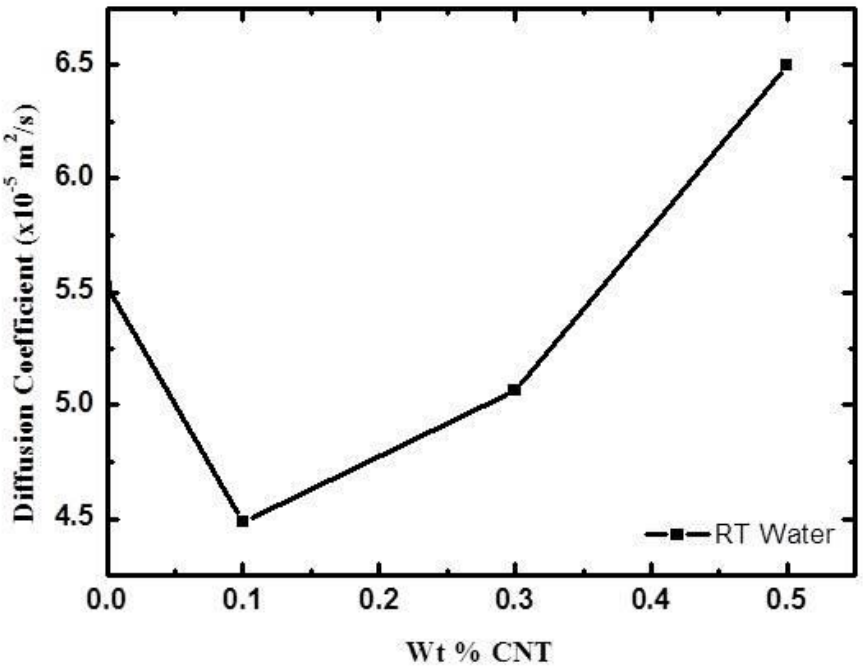


Fig. 15: comparing diffusivity of water molecules in different material systems conditioned at room temperature water

Here GFRP_0.1%CNT shows least diffusivity of water molecules into the composites and further diffusivity increases with CNT percentage, this is due to uniform dispersion CNT in the matrix phase as compared to the heterogeneous distribution of CNT in other cases, which increases the void spacing and, hence increases the diffusivity through the composite.

4.2) Effect of cold water(5°C) conditioning on different material systems(GFRP, GFRP-0.1%CNT, GFRP-0.3%CNT, GFRP-0.5%CNT)

4.2.1) Moisture ingression behaviour in different material systems.

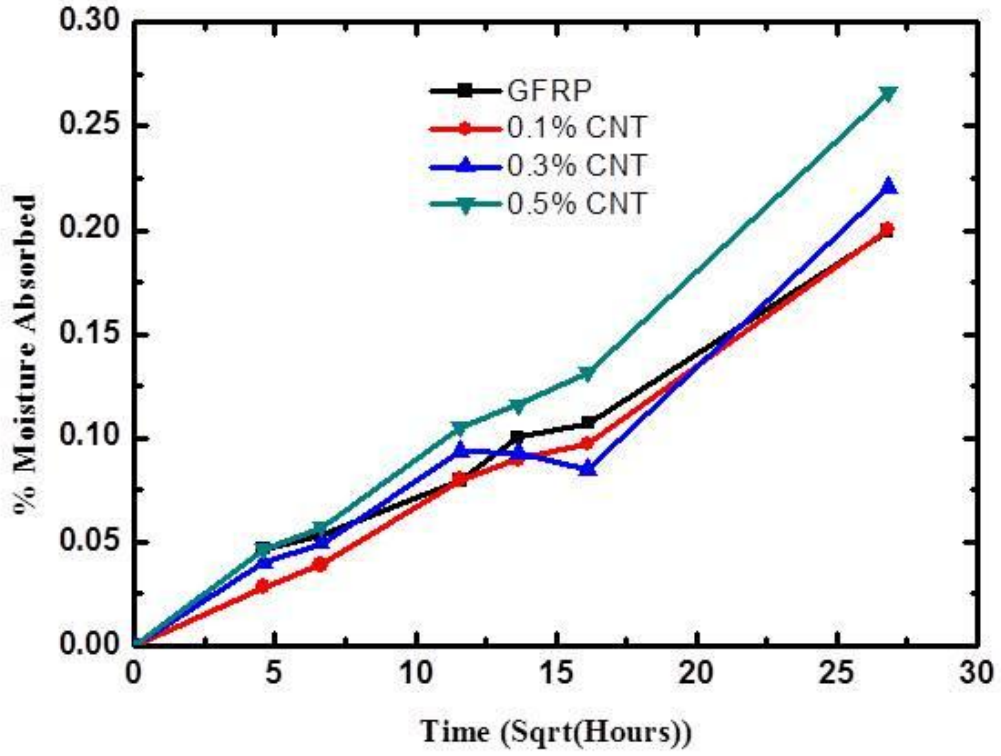
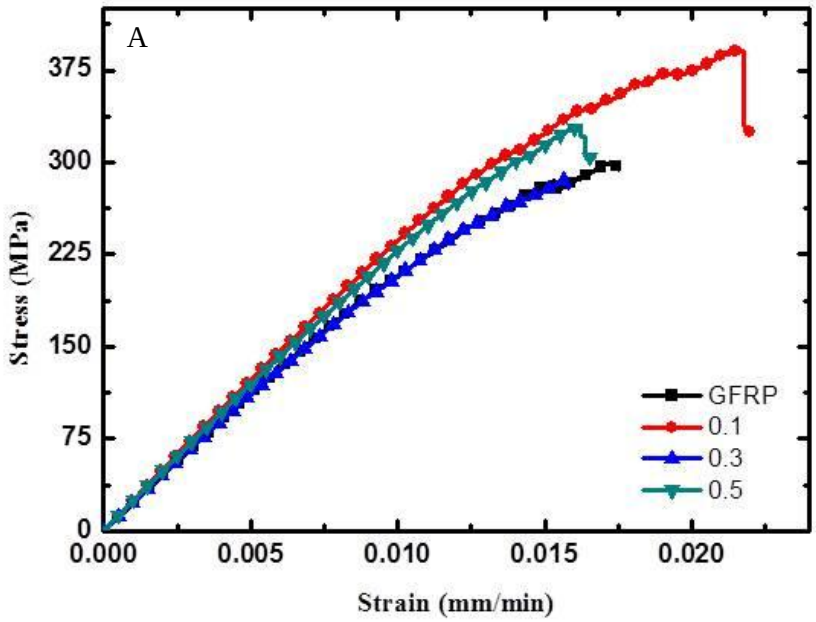


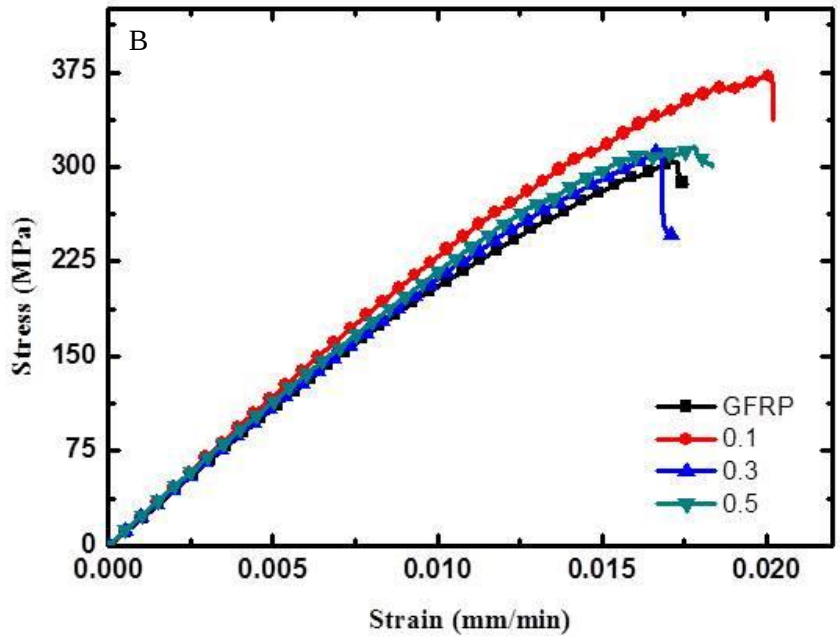
Fig. 16: Moisture absorption by different materials with increasing exposure time.

In this case, moisture absorbed by composites is less than in room temperature conditioning, as diffusion is a temperature dependent phenomena and varies directly with temperature. At low temperature, matrix hardening takes place which increase the cross-linking of chains, which decreases the free volume and hence reduces the uptake of moisture content.

Moisture absorbed by 0.5%CNT is higher than others, due to agglomeration of CNTs in the composites or non-uniform dispersion of CNTs in contrast to 0.1%CNT which shows least absorption due to uniform dispersion.

4.2.2) Effect of moisture absorption on mechanical properties with increasing exposure time.





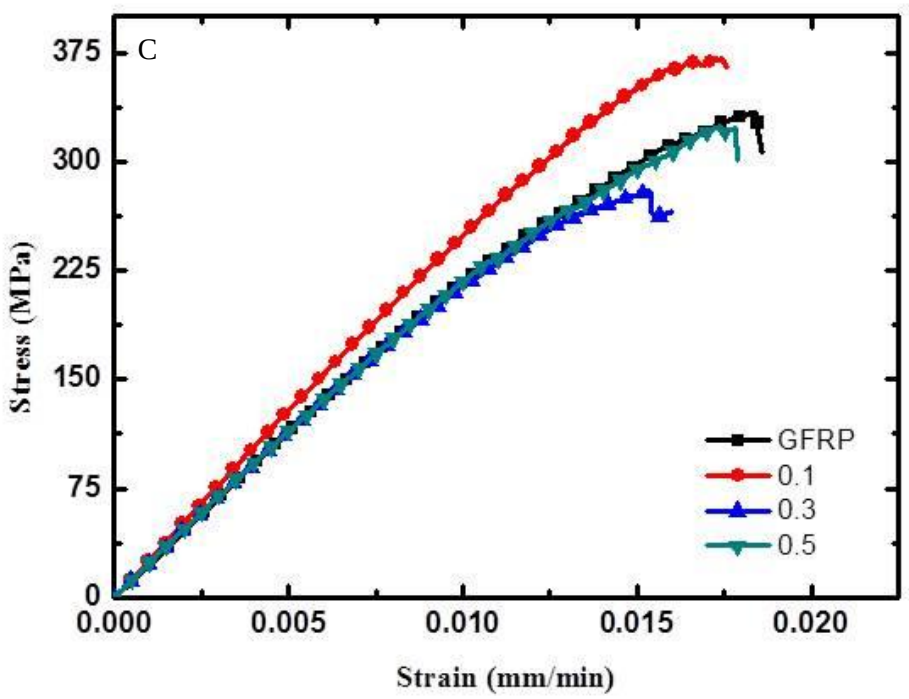
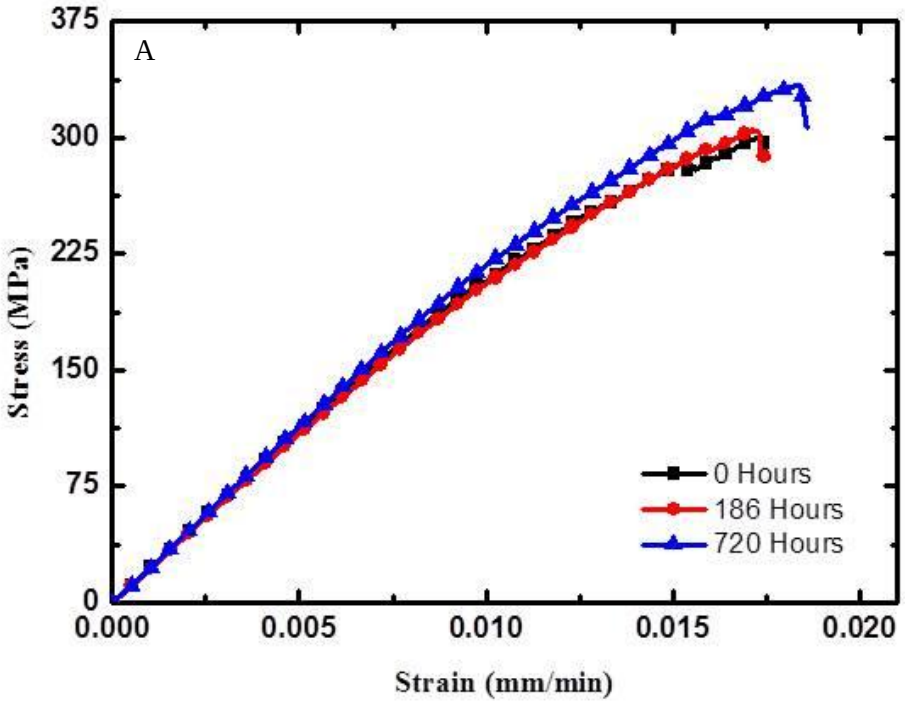
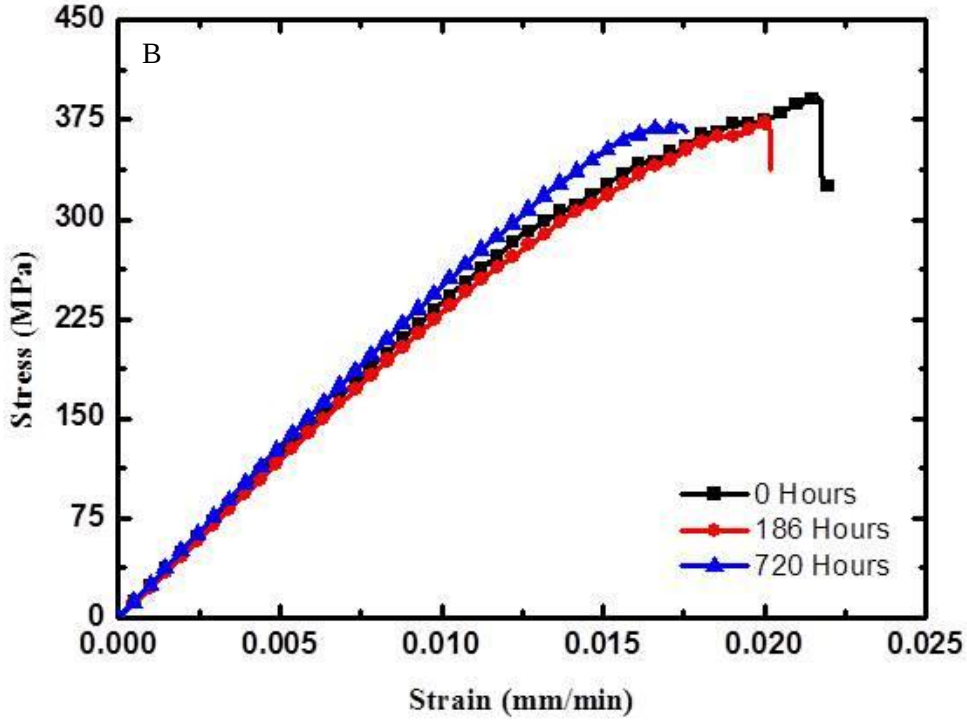


Fig. 17: Stress-strain diagrams of different material systems at different exposing time in cold water (A) without conditioning (B) 186 hours (C) 720 hours

In all the cases, GFRP-0.1%CNT exhibits higher strength at failure strain. With increasing exposing time in cold water(low temperature), materials experience brittleness due to matrix hardening resulting low strain at failure as compared to room temperature water. Higher strength of GFRP-0.1%CNT is due to uniform dispersion, which increases the surface area and, hence better load transfer from matrix to fibre.

4.2.3) Effect of exposure time on mechanical properties of individual material systems.





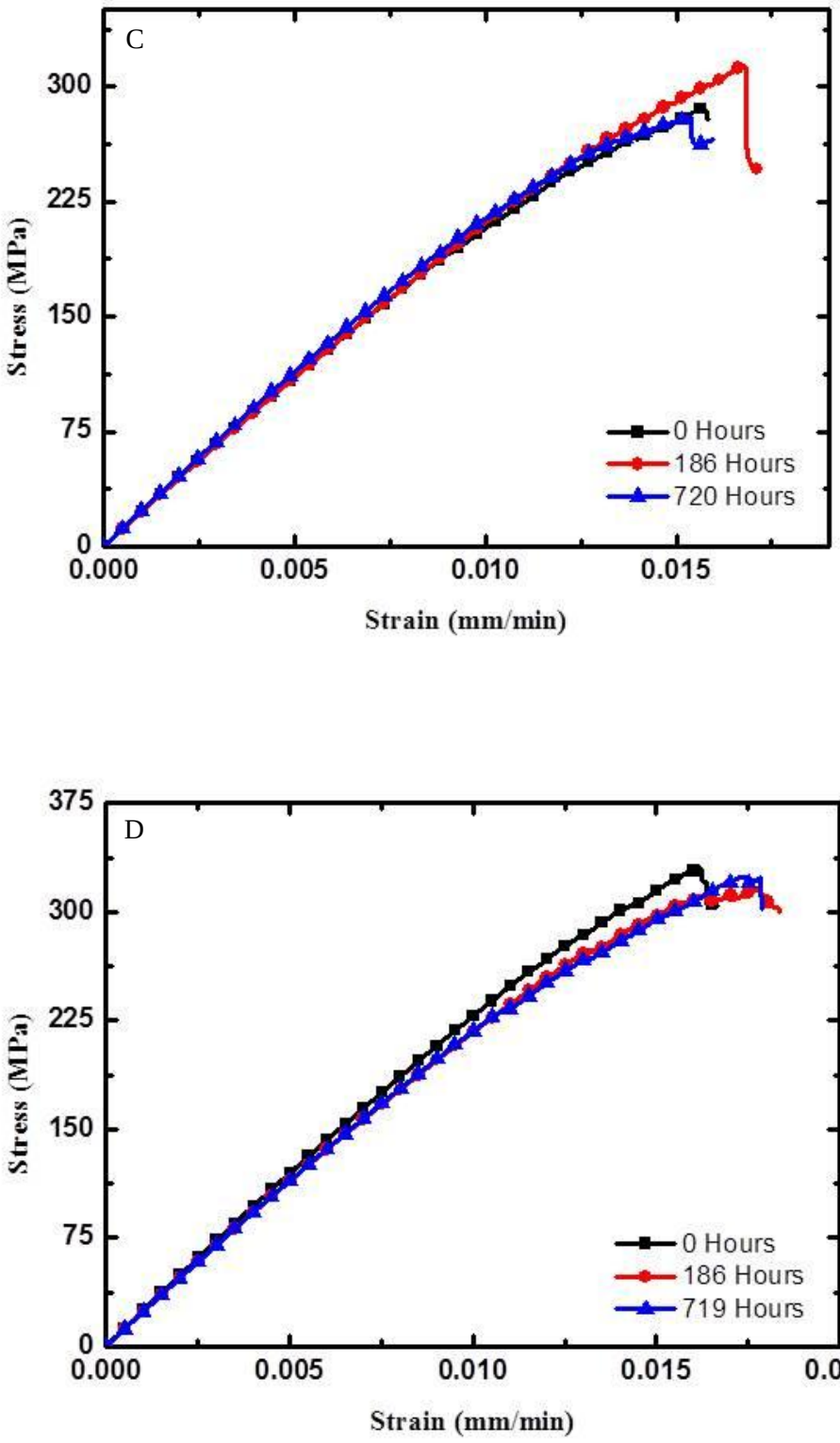
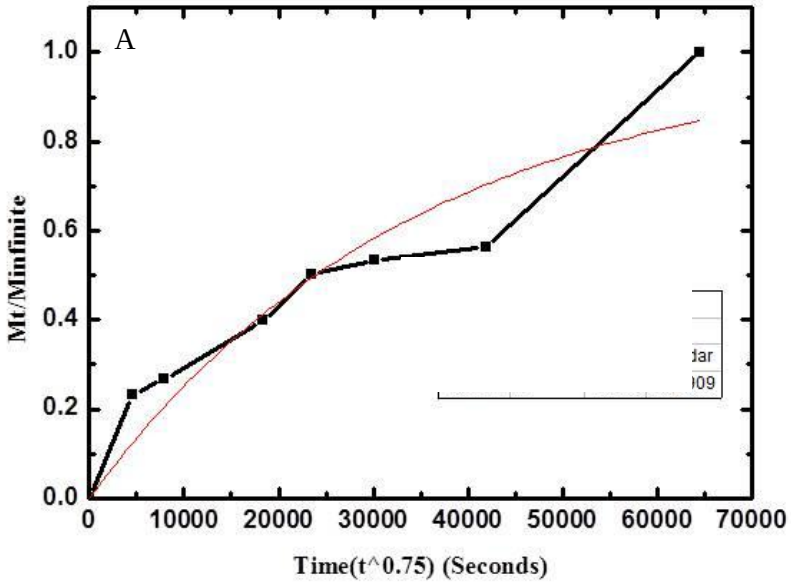


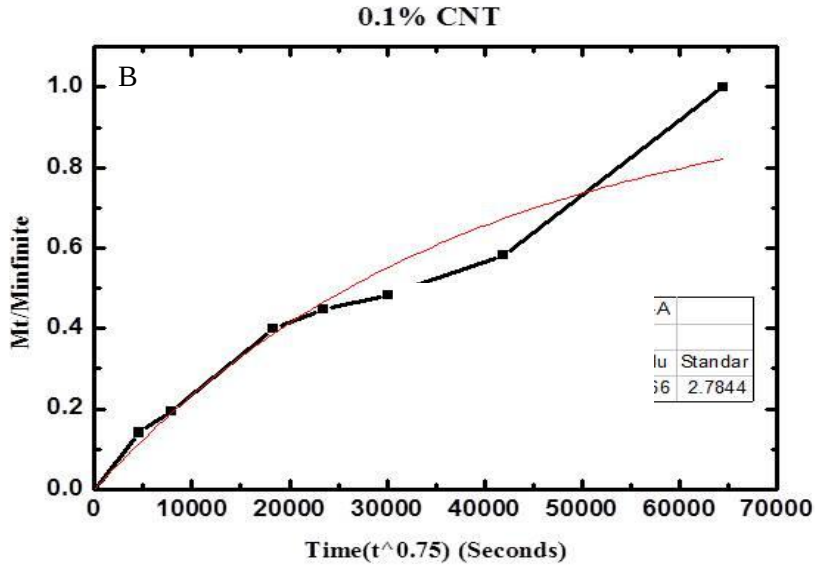
Fig. 18: Stress –strain diagrams at different exposing time in cold water (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

With increasing exposing time, inferior properties are observed in all materials due to some amount of moisture absorption which causes hydrolysis, plasticization and leaching. 0.3%CNT shows better properties when immersed in 5˚C water for 186 hours. This may be due to cancelling effect of the compressive stresses generated during curing know as curing stresses, the tensile stresses generated during the contraction of composite in cold water and the tensile stresses generated due to swelling.

4.2.4) Moisture ingression kinetics of different material systems



0.1% CNT



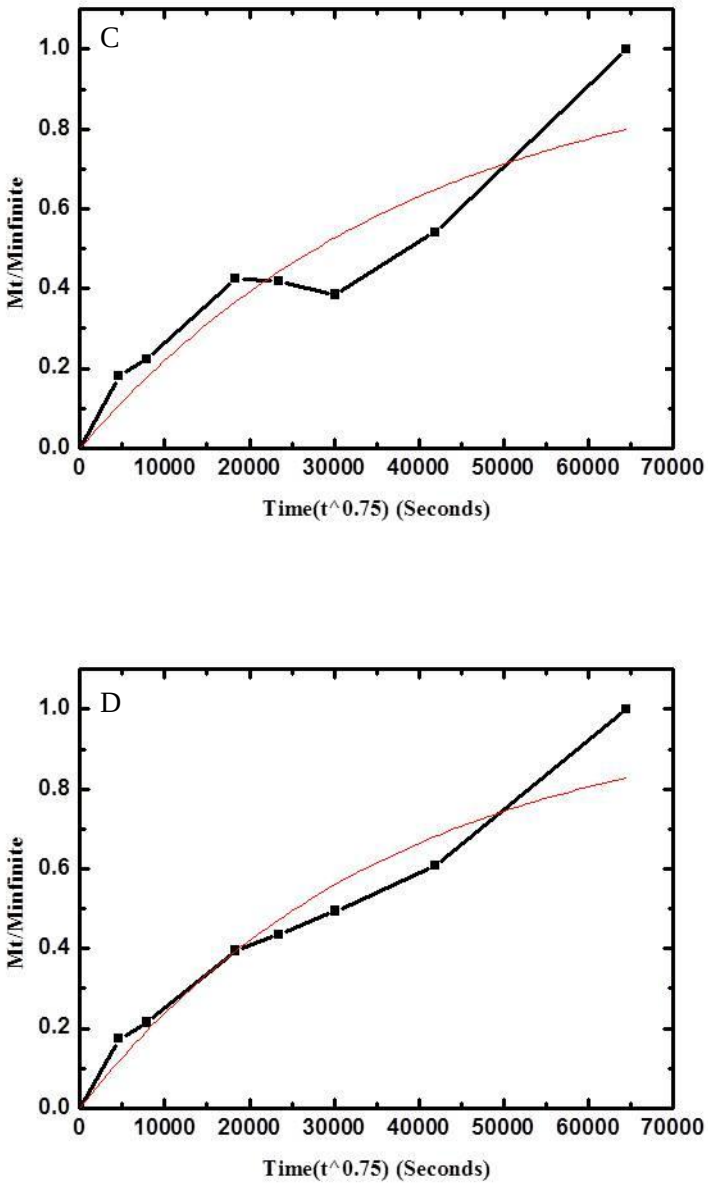
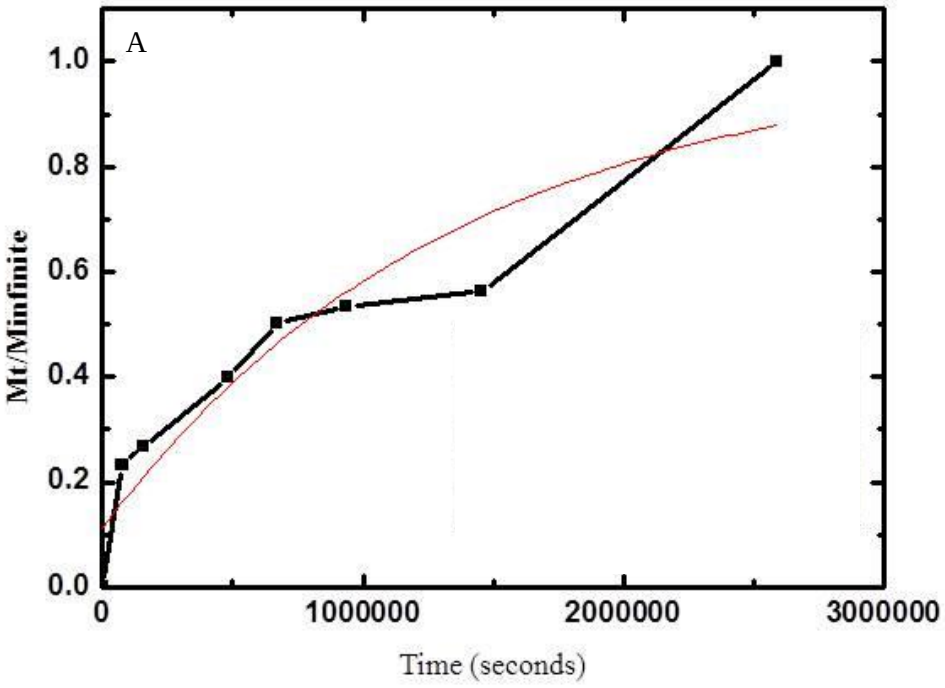


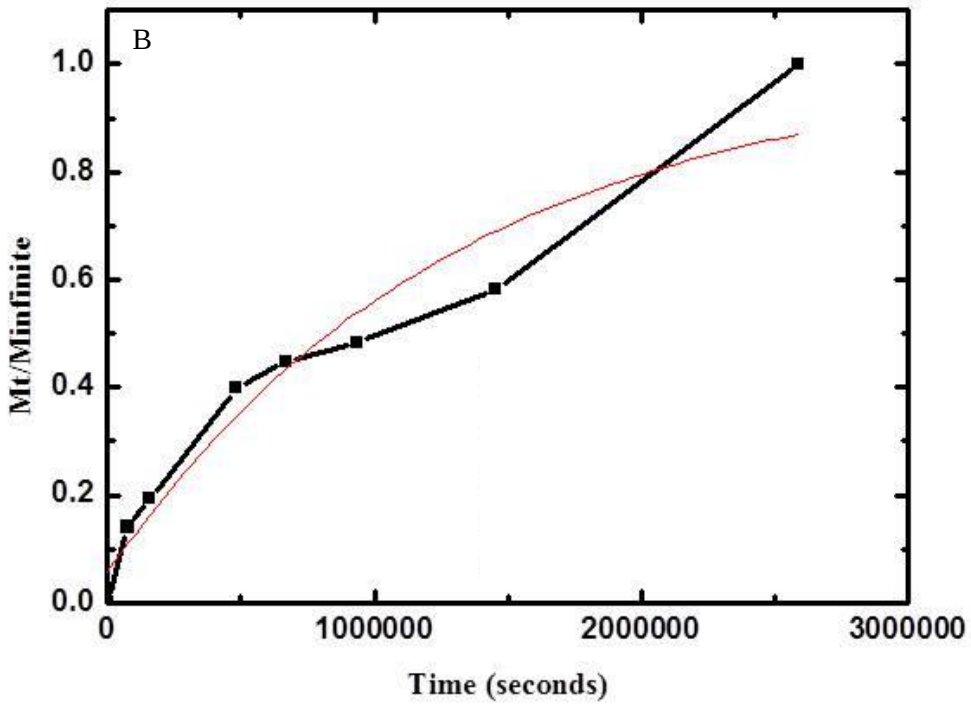
Fig. 19: Fick's Moisture diffusion fitting curves obtained (conditioned in cold water) (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

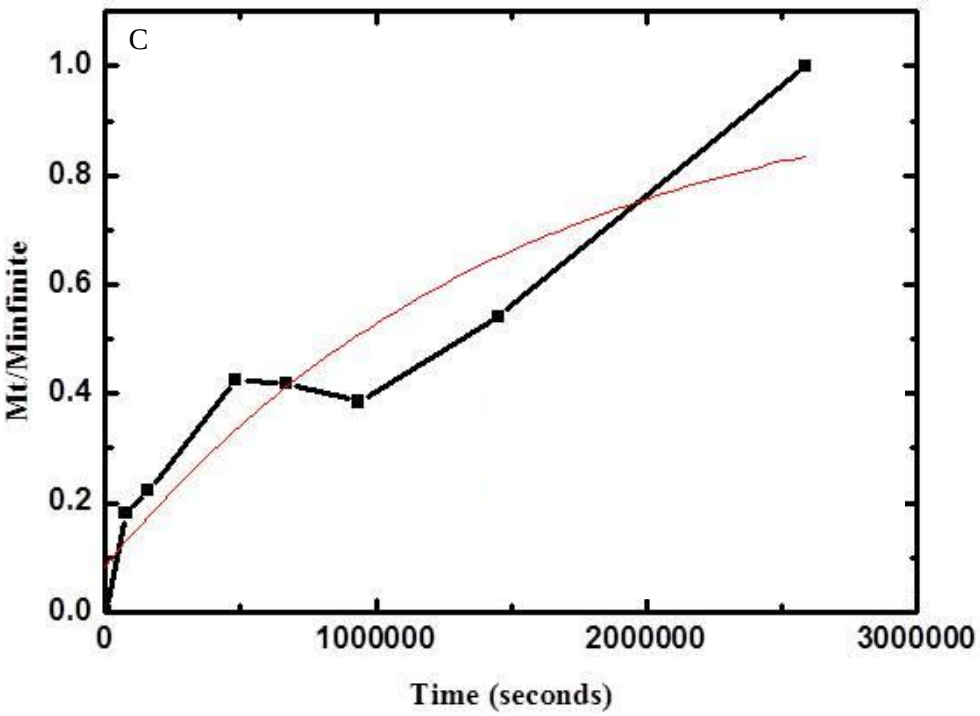
In fig (B) i.e GFRP-0.1%CNT shows linear curve initially which follows Fickian behaviour but after that it seem to follow hindered diffusion or may be other diffusion that may be confirmed on further conditioning for longer period of time which is also shown by other material systems. The Fickian curve is fitted using equation no. 5 in origin, and diffusivity is calculated for different systems.

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \quad (5)$$

The coefficient of regression in Fickian fitting is much lower when the samples are exposed to 5˚C water as compared to when the samples are exposed to 35˚C water, which shows that Fickian behaviour is evident at higher temperatures.







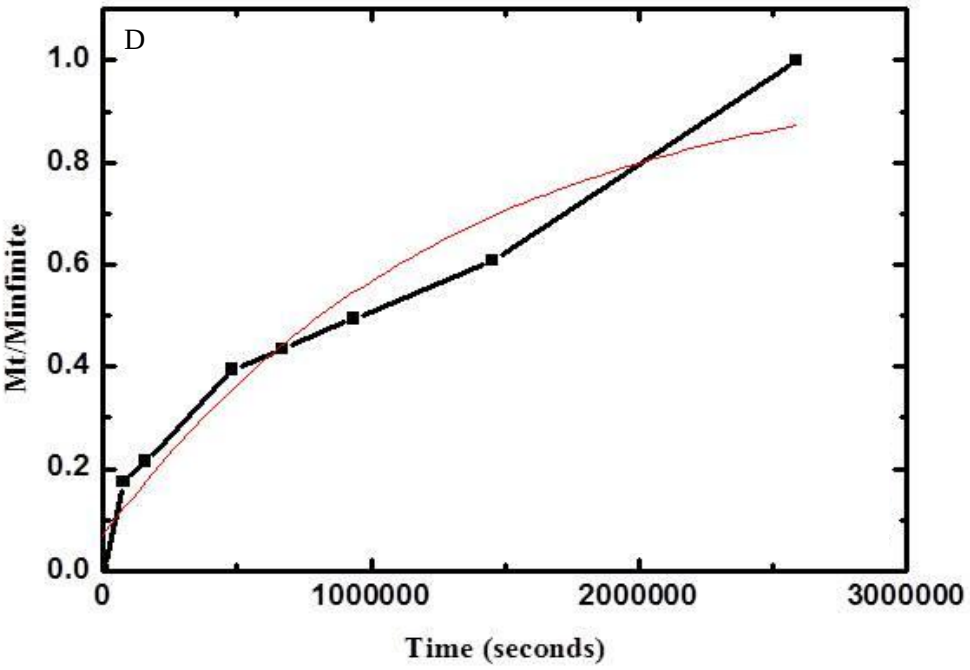


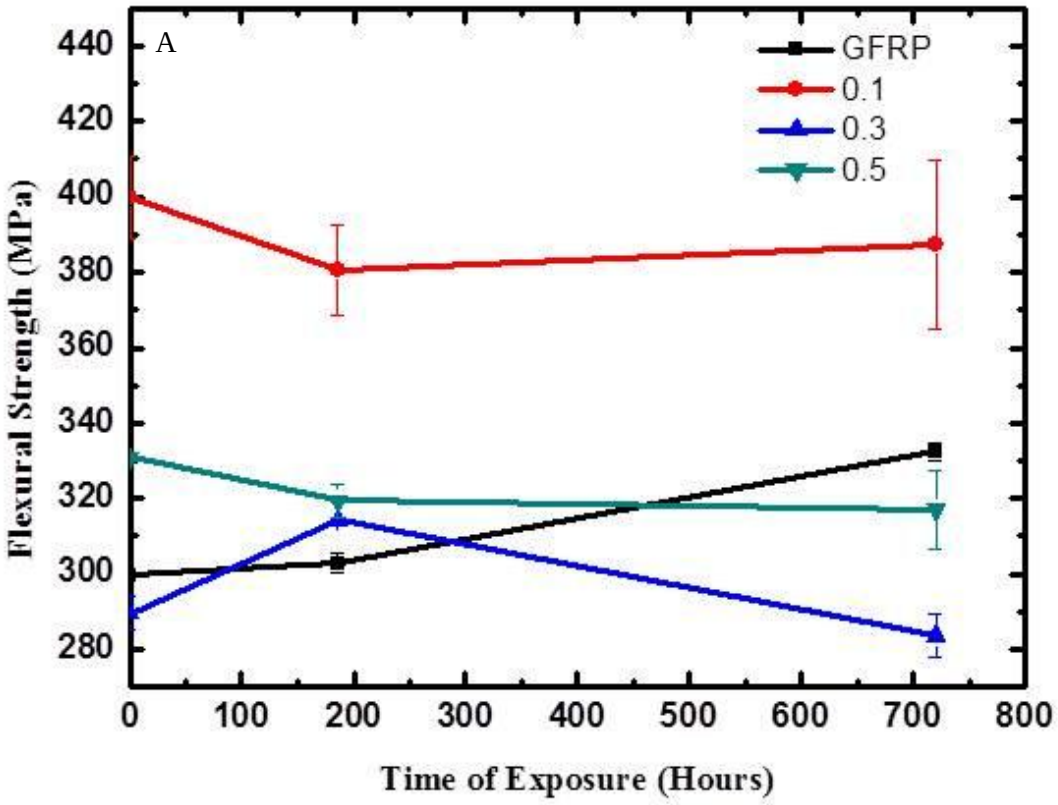
Fig. 20: Langmurian diffusion fitting curves obtained (conditioned in cold water) (A) GFRP (B) GFRP-0.1%CNT (C) GFRP-0.3%CNT (D) GFRP-0.5%CNT

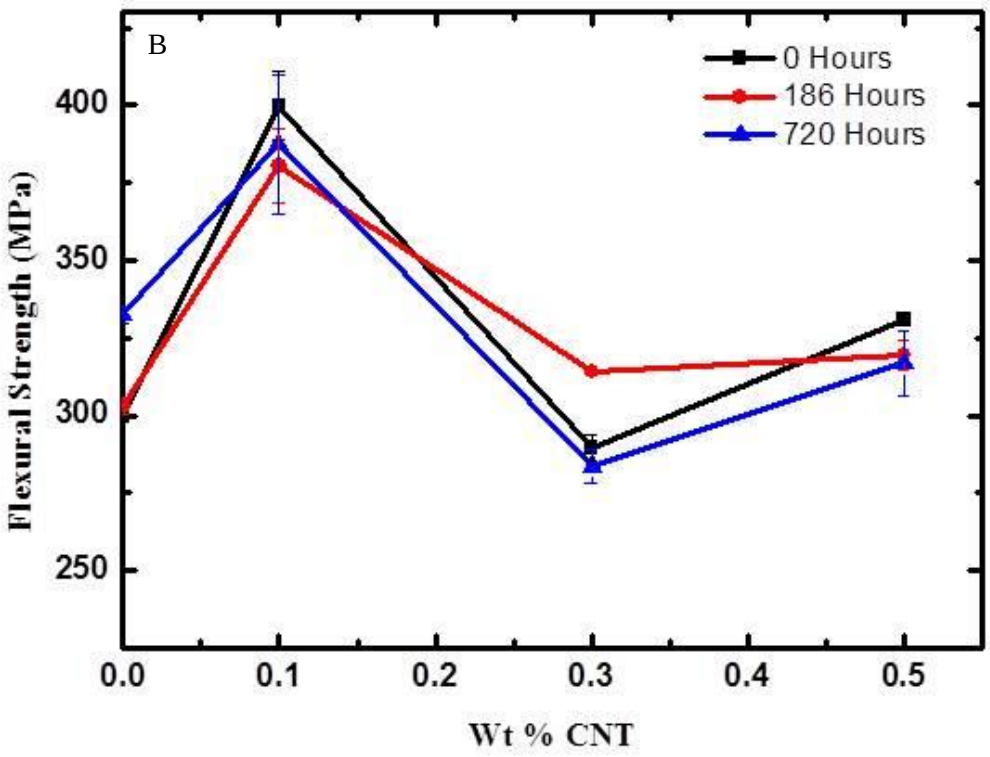
Langmurian curve is fitted in equation no. 12 using origin, and the values of alpha and gamma are calculated.

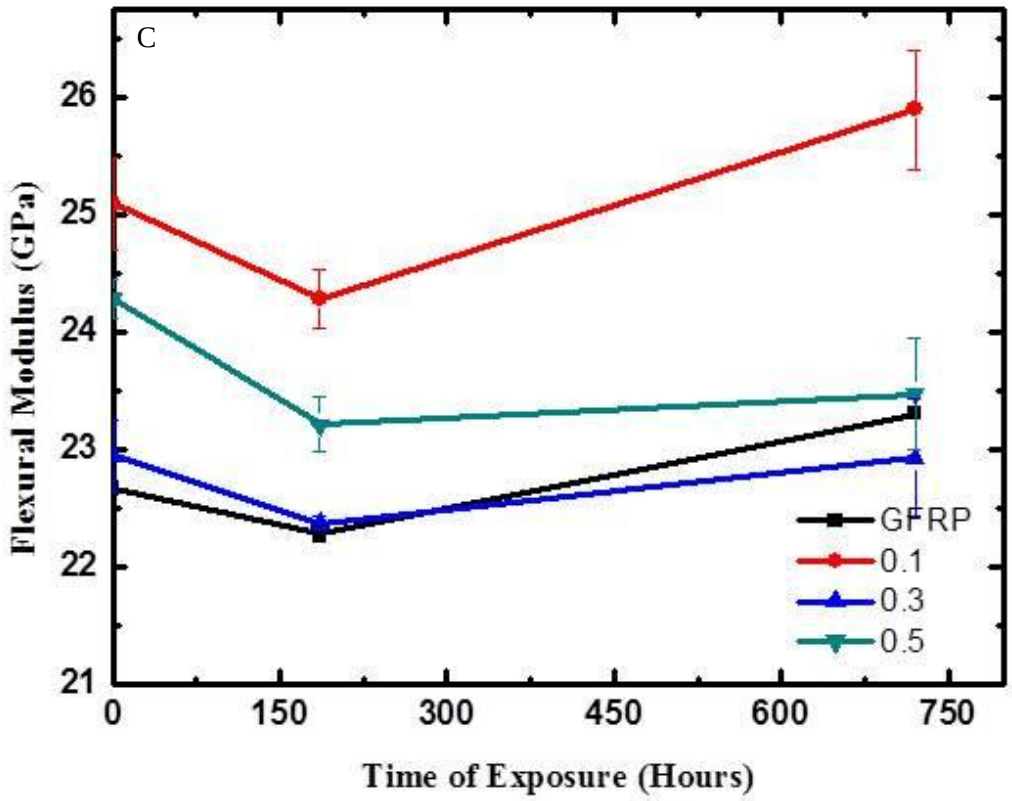
$$\frac{M_t}{M_\infty} \approx 1 - \frac{\gamma}{\gamma+\beta} e^{-\beta t} \; ; \; 2\gamma, 2\beta \ll \kappa, t \gg \frac{1}{\kappa} \quad (12)$$

It is reported by many researchers that Langmurian diffusion model is more accurate than Fick's diffusion model.

4.2.5) Effect of moisture ingression on flexural strength and flexural modulus




B
0 Hours
186 Hours
720 Hours
Flexural Strength (MPa)
400
350
300
250
0.0
0.1
0.2
0.3
0.4
0.5
Wt % CNT


C
Flexural Modulus (GPa)
26
25
24
23
22
21
0
150
300
450
600
750
Time of Exposure (Hours)
GFRP
0.1
0.3
0.5

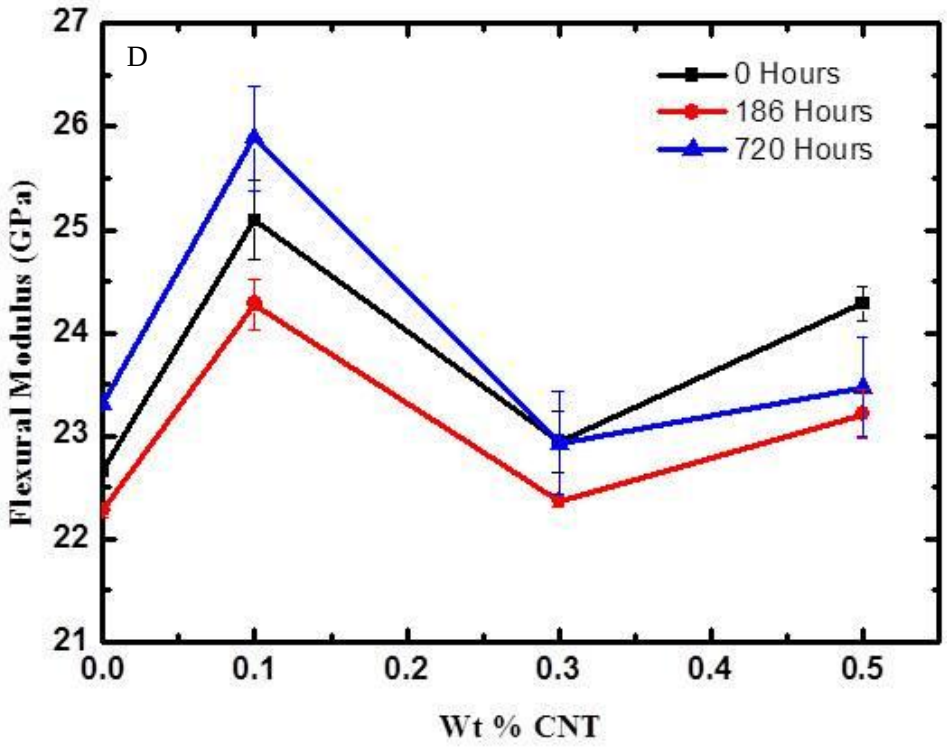


Fig. 21: At cold water conditioning (A) Flexural strength vs exposure time (B) flexural strength vs wt%.CNT (C) flexural modulus vs exposure time (D) flexural modulus vs wt%.CNT

The significant change in flexural strength and modulus is not observed on short conditioning time in cold water ,it may be observed in longer exposing time. In fig (D), it is observed that GFRP-0.1%CNT exhibits higher flexural modulus at relatively higher exposing time but it may show deleterious effects on exposing for much longer period of time. In case of 5˚C water also 0.1%CNT shows maximum flexural strength and modulus at any time and temperature.

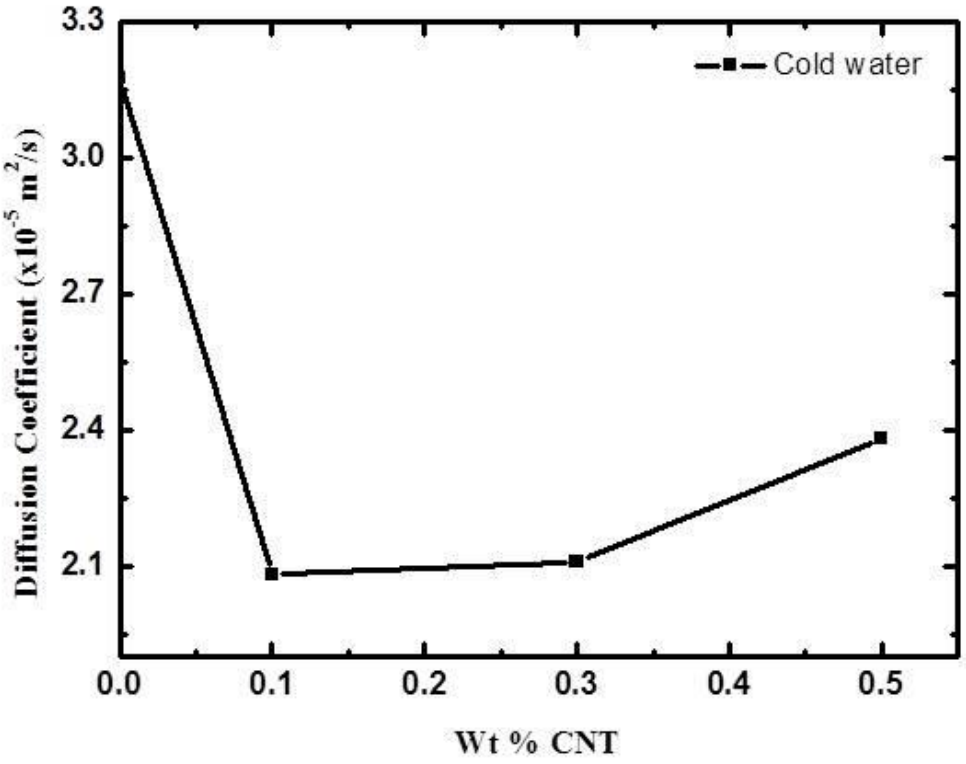


Fig.22: comparing diffusivity of water molecules in different material systems conditioned in cold water

It is observed that addition of CNTs in GFRP reduces the diffusivity of water molecules into the composites and the least diffusivity is shown by GFRP-0.1%CNT. In case of 5˚C water the available amount of free volume is reduced due to contraction effect of 5˚C water and hence the diffusivity of water molecules through the composite becomes more difficult. The diffusivity of 0.1%CNT in case of 35˚C water was 100% more as compared to that, in case of 5˚C water.

4.3) Effect of hygro-thermal conditioning on GFRP composites

4.3.1) Moisture ingression behaviour in GFRP composites

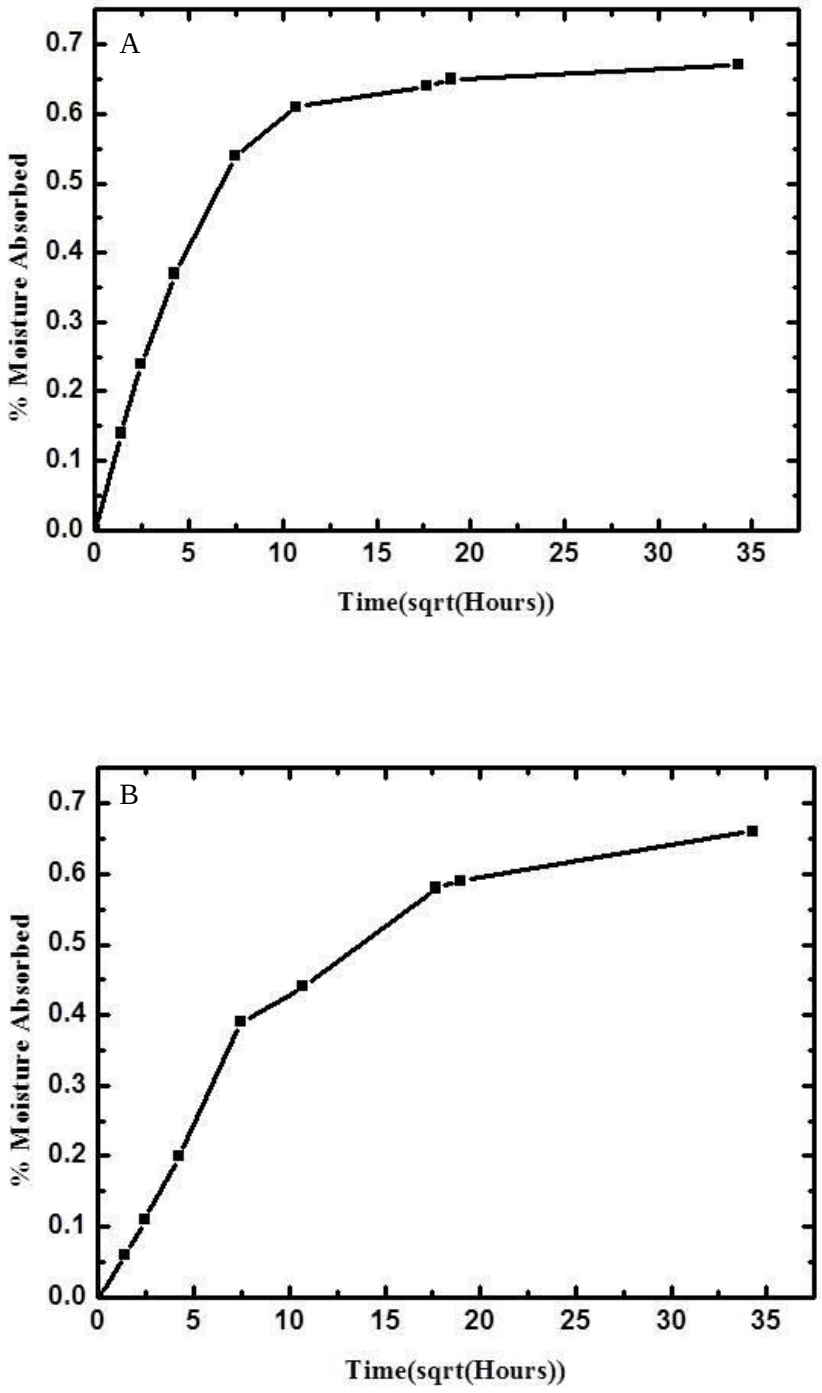
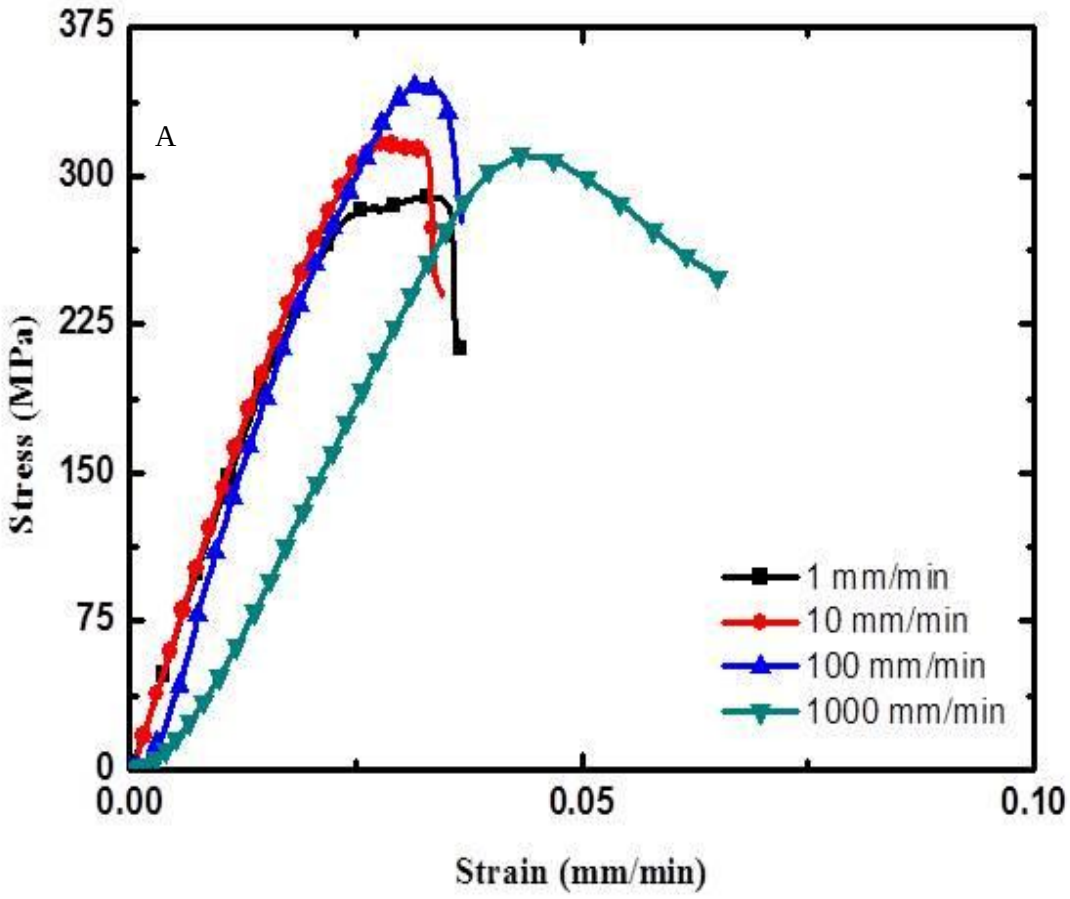


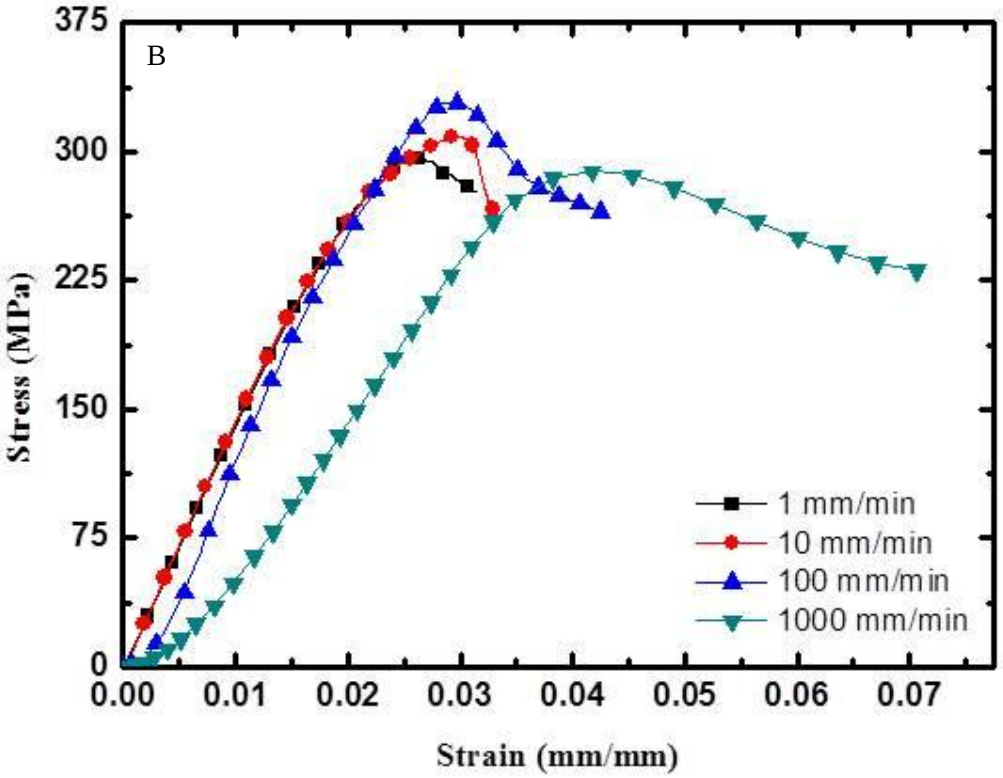
Fig.23: Moisture absorption kinetics of (A) GFRP (ILSS) (B) GFRP (flexural) conditioned at 70˚C and 95%RH.

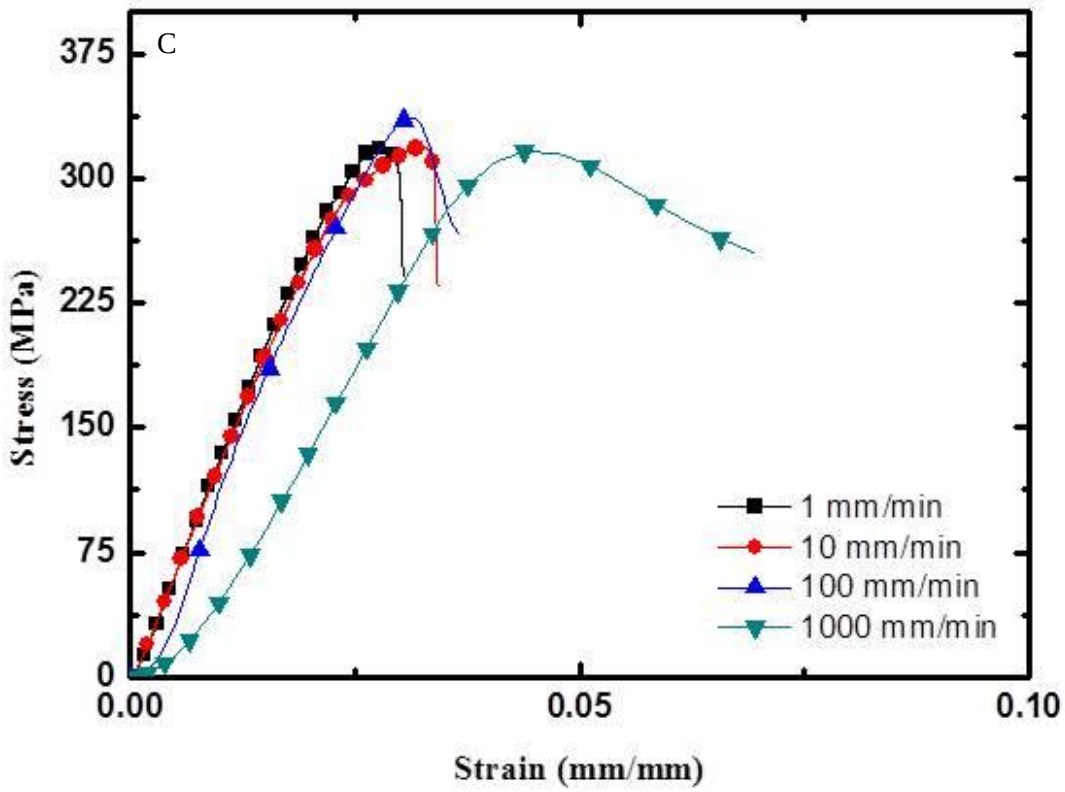
Fig.23: Shows the percentage of moisture absorbed with increase in time. It can be seen from the figure that the absorption of moisture during the early stages of experiment is very high

and then attains a pseudo equilibrium. ILSS samples follow Fick's law of diffusion whereas flexural samples follow dual phase diffusion model. The flexural curves are below the ILSS curves at any point of time and have the same saturation level. This suggests that the absorption kinetics depends on the dimension of the samples i.e. surface to volume ratio, but have the same percentage of moisture absorbed in a particular environment. ILSS samples have higher surface by volume ratio as compared to flexural samples and hence absorb faster as compared to flexural samples.

4.3.2) Effect of moisture absorption on mechanical properties of GFRP composite




B
375
300
225
150
75
0
Stress (MPa)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
Strain (mm/mm)
1 mm/min
10 mm/min
100 mm/min
1000 mm/min


C
375
300
225
150
75
0
Stress (MPa)
0.00
0.05
0.10
Strain (mm/mm)
1 mm/min
10 mm/min
100 mm/min
1000 mm/min

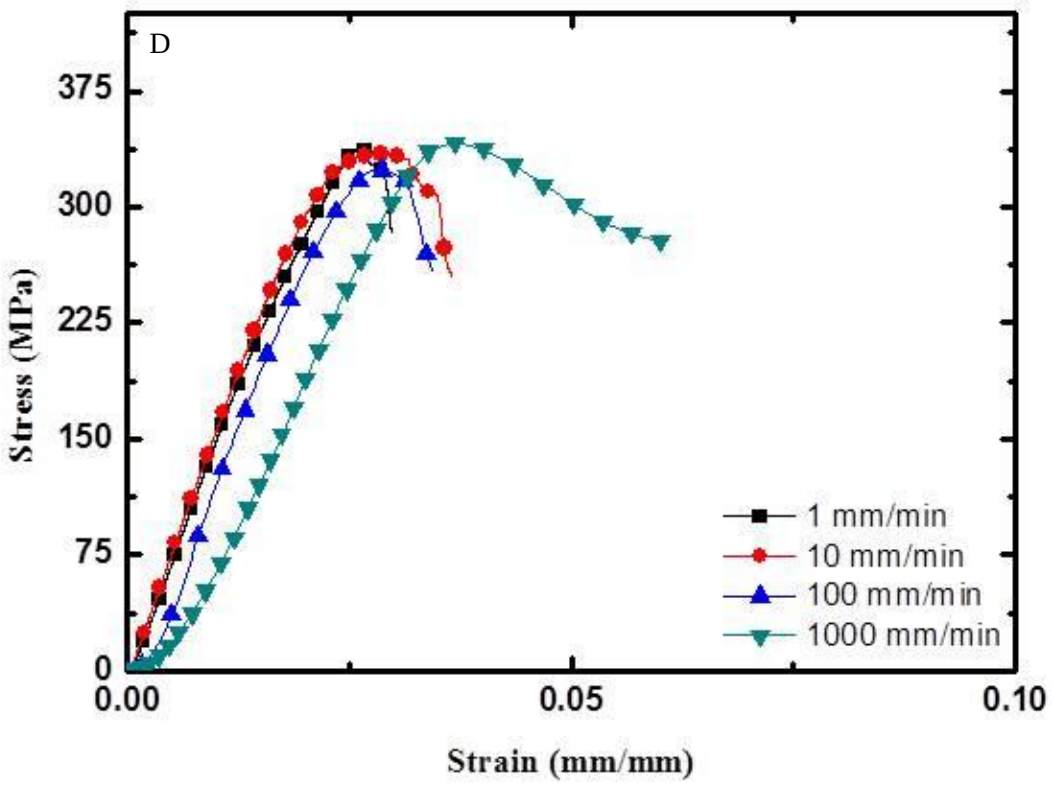


Fig 24: stress-strain diagrams of GFRP (A) without conditioning (B) 8 hours liquid N_2 dipped (C) exposed to moisture for 45 days (D) exposed to moisture for 45 days with 8 hours liquid N_2 dipped

Fig.24: shows the stress vs strain graphs for various loading rates. The maximum flexural stress in all the cases is obtained at a loading rate of 100mm/min. In case of 1mm/min, the matrix has enough time to transfer the load to the fibres and the failure mode is due to delamination/de-bonding. At 10mm/min and 100mm/min loading rate, the failure mode is due to fibre breakage and fibre pull out which requires very high energy as compared to delamination/de-bonding. Hence, 10mm/min and 100mm/min show higher maximum flexural strength as compared to 1mm/min. Finally, at 1000mm/min there would be impact loading and the failure would be due to matrix cracking which requires less energy. Matrix ductility becomes limiting factor and efficient load transfer is not possible due to matrix cracking. Hence, 1000mm/min has lower maximum flexural strength as compared to 100mm/min.

4.3.3) Moisture ingression kinetics of GFRP composites

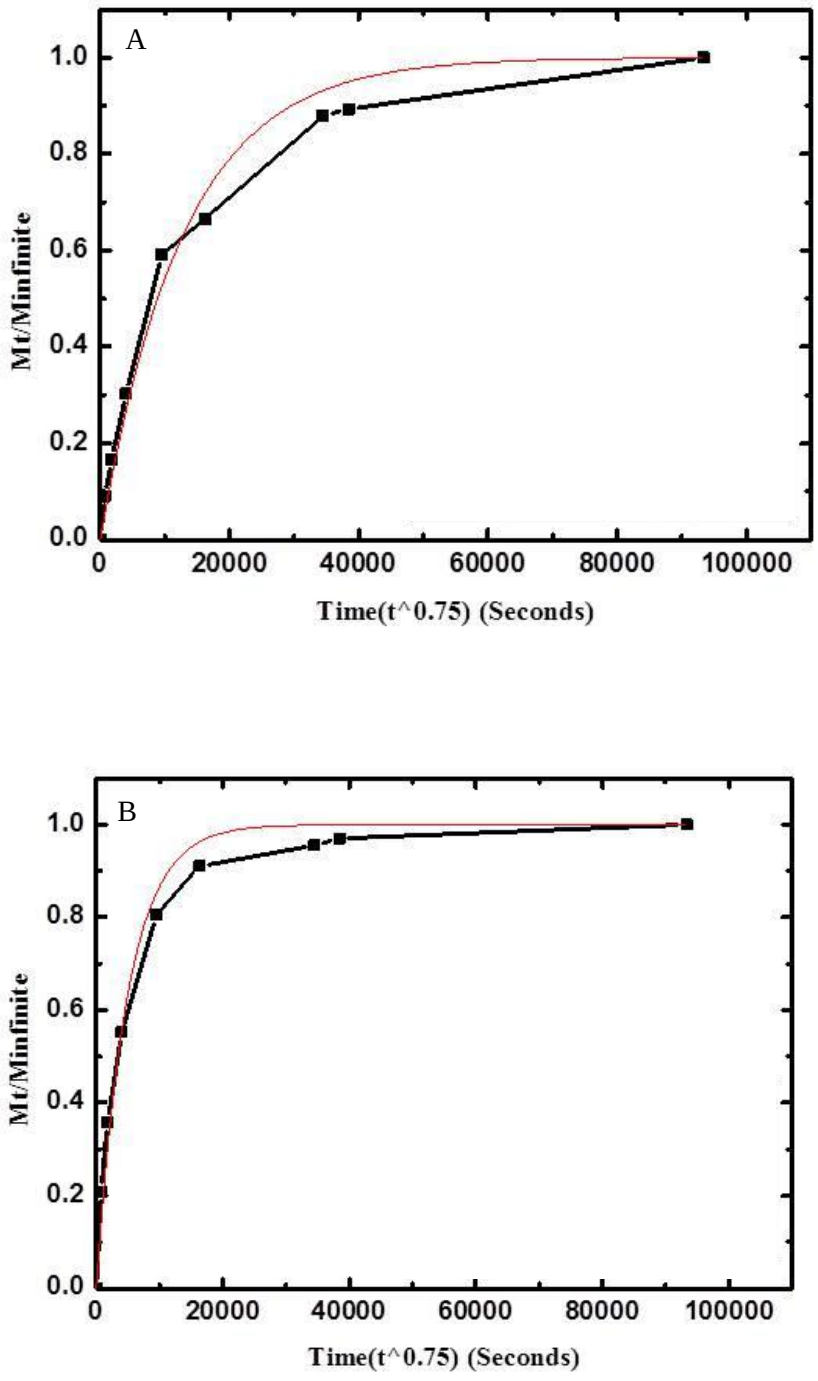


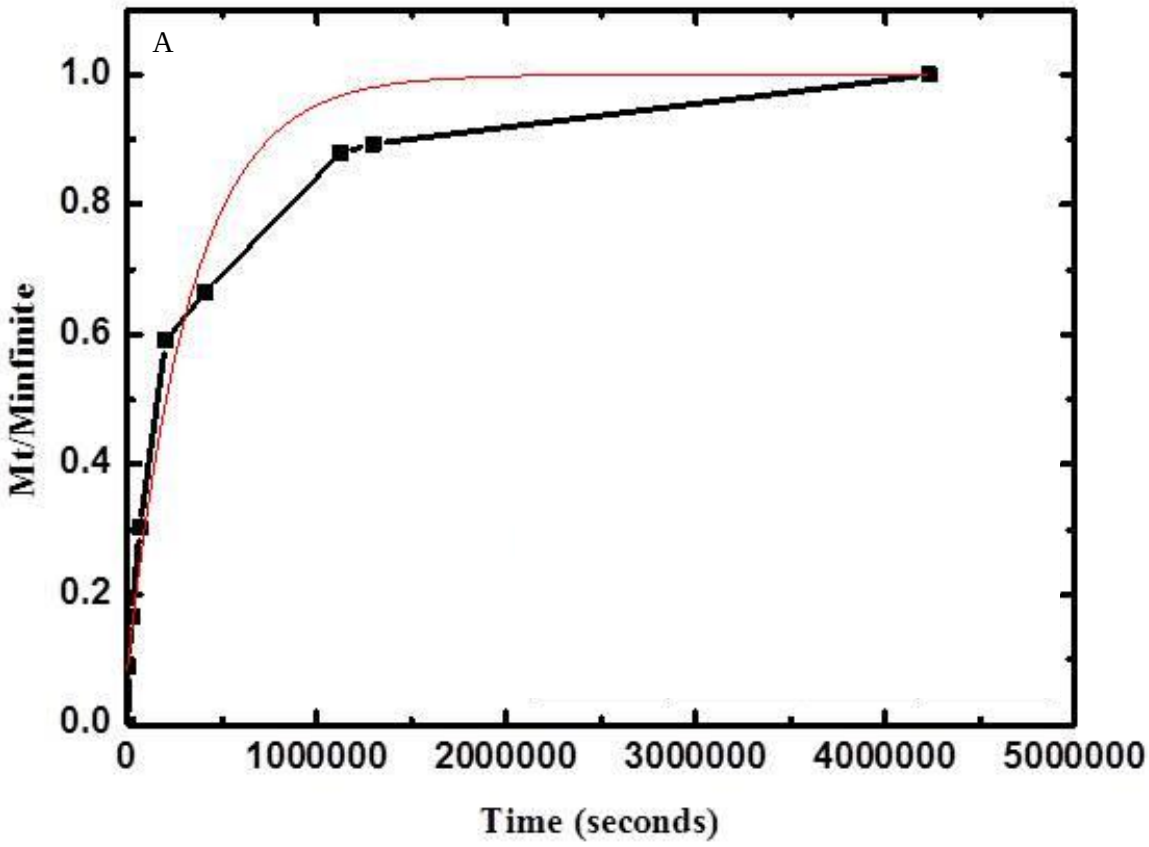
Fig 25: Fick's Moisture diffusion fitting curves obtained (conditioned at 95%RH and 70˚C) (A) GFRP (Flexural samples) (B) GFRP (ILSS samples)

In fig (A) and (B) i.e. GFRP (Flexural) and GFRP (ILSS) shows linear curve initially which follows Fickian behaviour but after that it seem to follow hindered diffusion or may be other

diffusion that may be confirmed on further conditioning for longer period of time. The Fickian curve is fitted using equation no. 5 in origin, and diffusivity is calculated for different systems.

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-7.3\left(\frac{Dt}{h^2}\right)^{0.75}\right] \quad (5)$$

The coefficient of regression in Fickian fitting is lower when the samples are flexural as compared to when the samples are ILSS, which shows that Fickian behaviour is evident in ILSS samples.



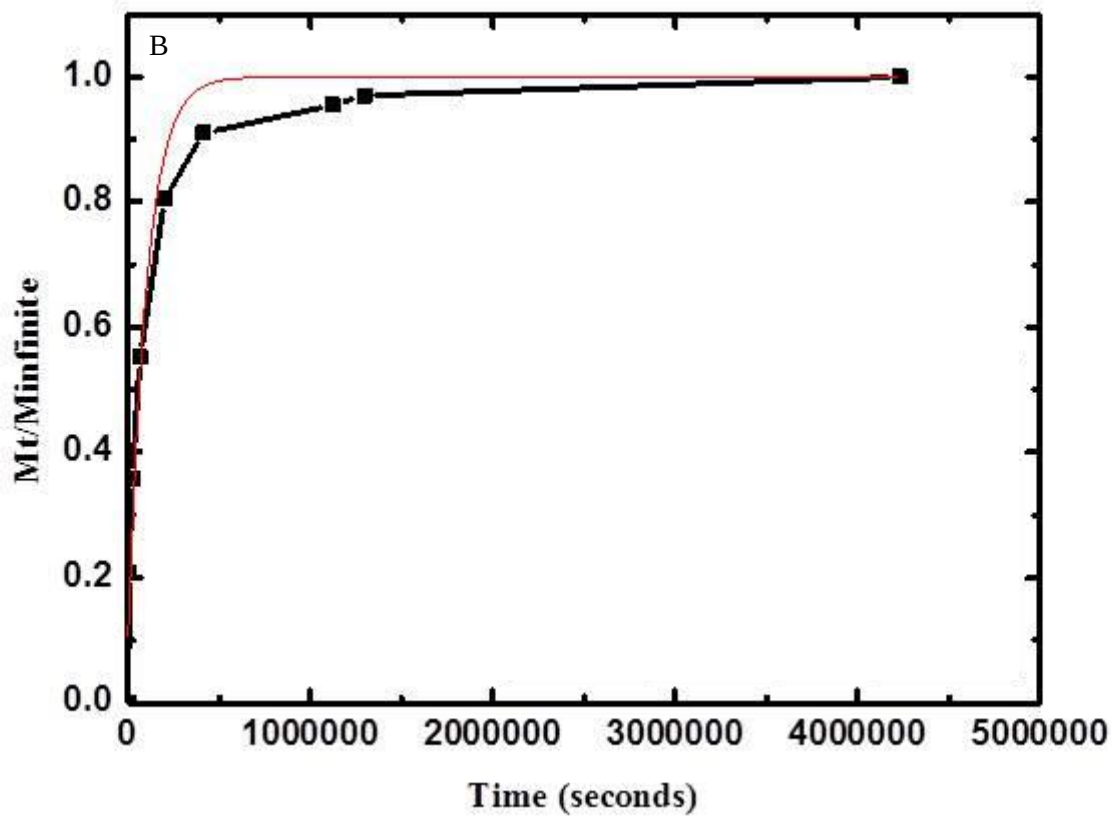


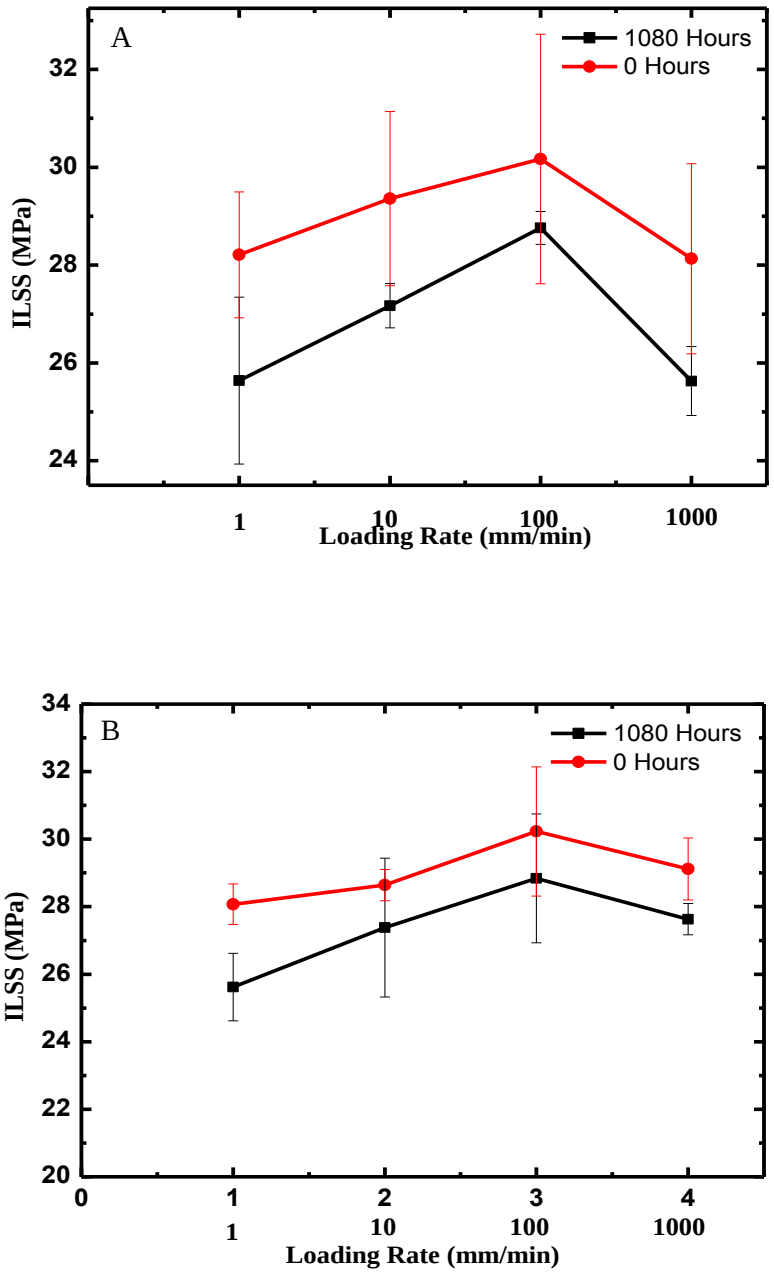
Fig 26: Langmurian diffusion fitting curves obtained (conditioned at 95%RH and 70˚C) (A) GFRP (Flexural samples) (B) GFRP (ILSS samples)

Langmurian curve is fitted in equation no. 12 using origin, and the values of alpha and gamma are calculated.

$$\frac{M_t}{M_\infty} \approx 1 - \frac{\gamma}{\gamma+\beta} e^{-\beta t} \; ; \; 2\gamma, 2\beta \ll \kappa, t \gg \frac{1}{\kappa} \quad (12)$$

It is reported by many researchers that Langmurian diffusion model is more accurate than Fick's diffusion model.

4.3.4) Effect of loading rates on the moisture conditioned GFRP composites



(b)

Fig 27: Variation of ILSS with loading rates (A) moisture conditioned and liquid N_2 dipped for 8 hours (B) moisture conditioned for 45 days

The maximum ILSS in all the cases is obtained at a loading rate of 100mm/min. In case of 1mm/min, efficiency of load transfer to the fibres is much higher and the failure mode is due to delamination/de-bonding. At 10mm/min and 100mm/min loading rate, the failure mode is due to fibre breakage and fibre pull out which requires very high energy as compared to

delamination/de-bonding. Hence, 10mm/min and 100mm/min show higher maximum ILSS as compared to 1mm/min. Finally, at 1000mm/min there would be impact loading and the failure would be due to matrix cracking which requires less energy. Matrix ductility becomes limiting factor and efficient load transfer to fibres is not possible. Hence, 1000mm/min has lower maximum flexural strength as compared to 100mm/min.

4.4) Micrographs:

4.4.1) No conditioning:

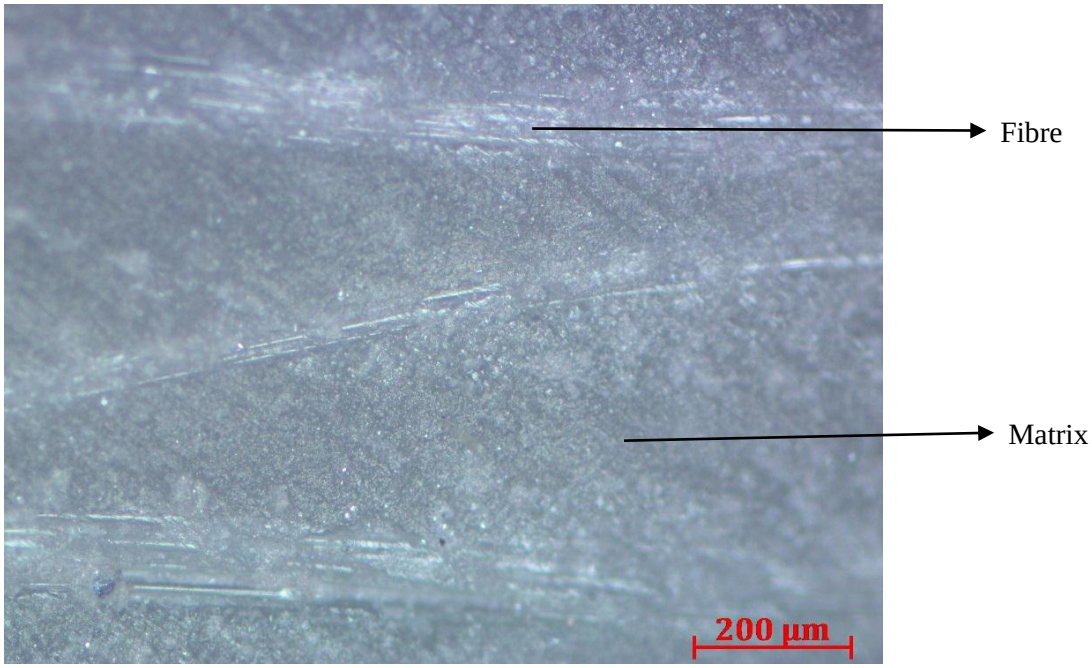
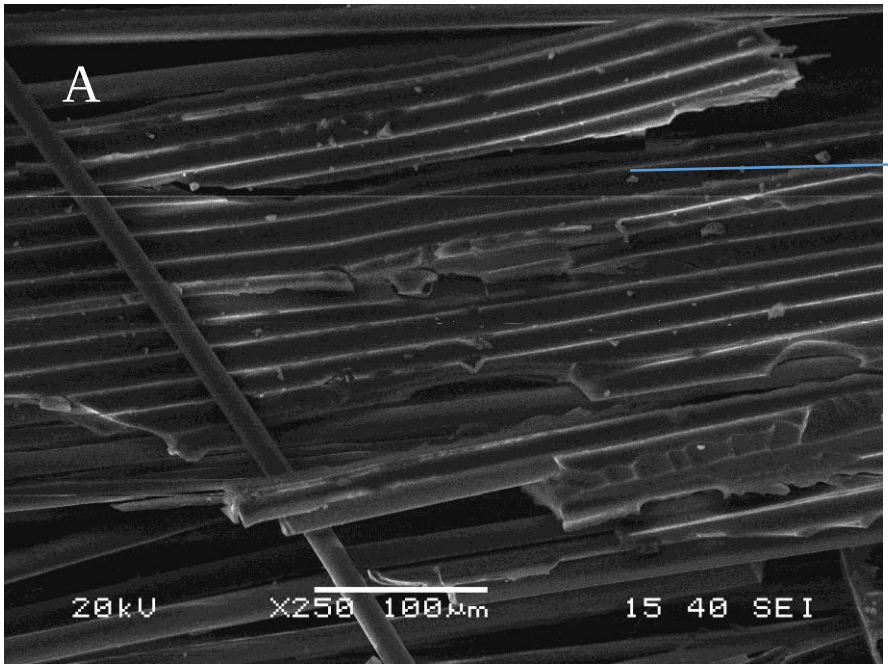


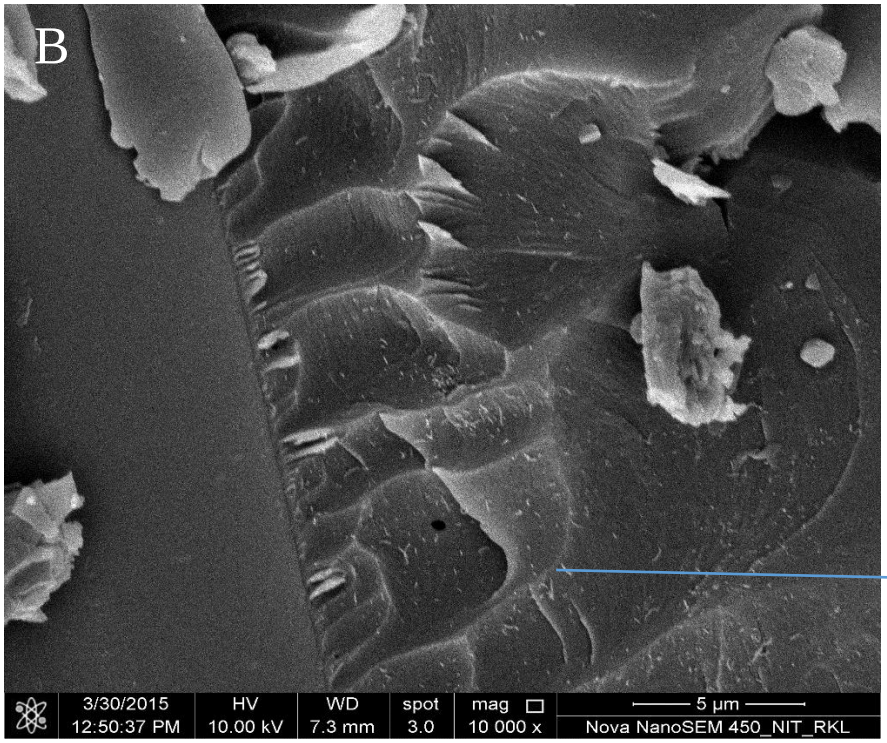
Fig. 28: Optical image of GFRP Composite

The above figure gives a brief idea about the orientation of fibres, which are wavy in nature.

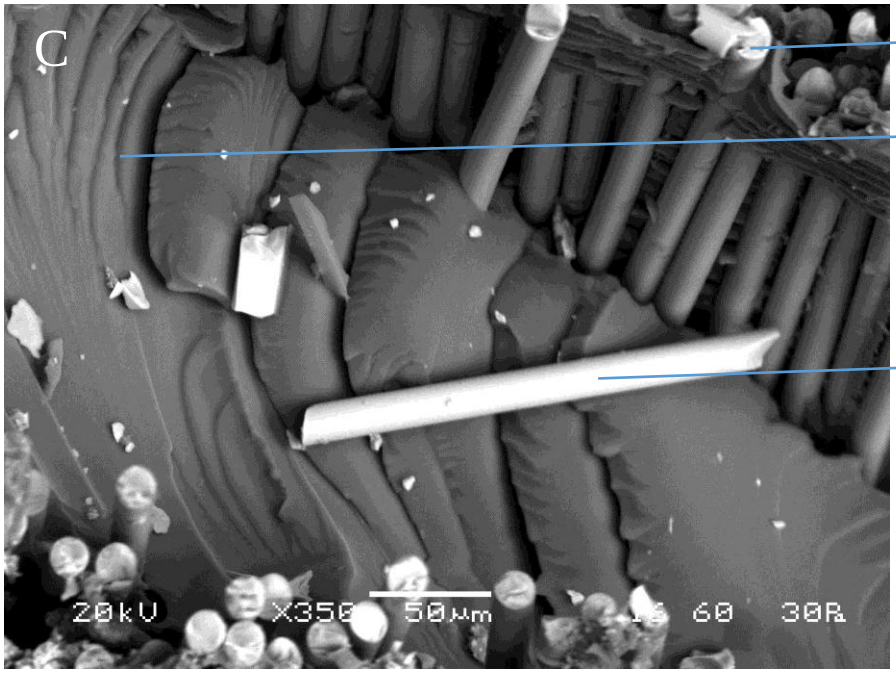
At fibre/matrix interphase, delamination is an important mode of failure in FRP composites materials in all environmental conditions. However, delamination and adhesion property at interphase are dependent on the environmental conditioning. From Fig: we see that there are three modes of failure (1) delamination, (2) Fibre Breakage and (3) Matrix Crack

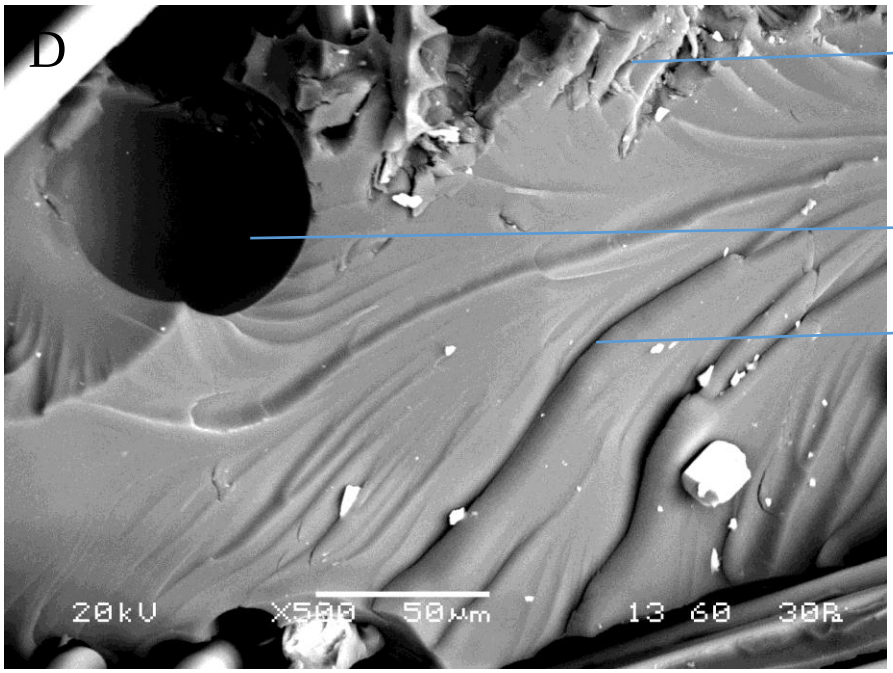


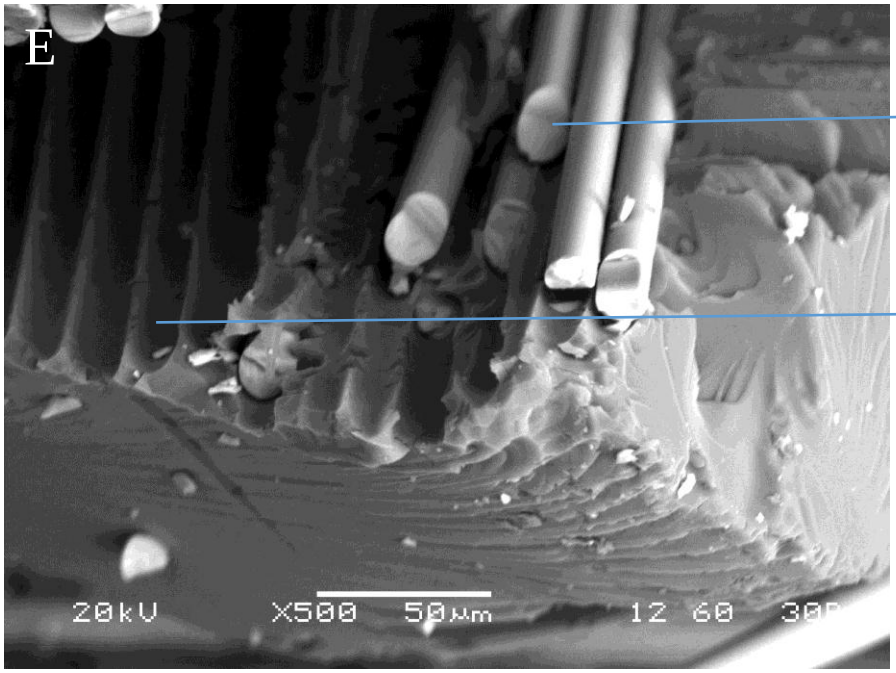
Fibre Imprints

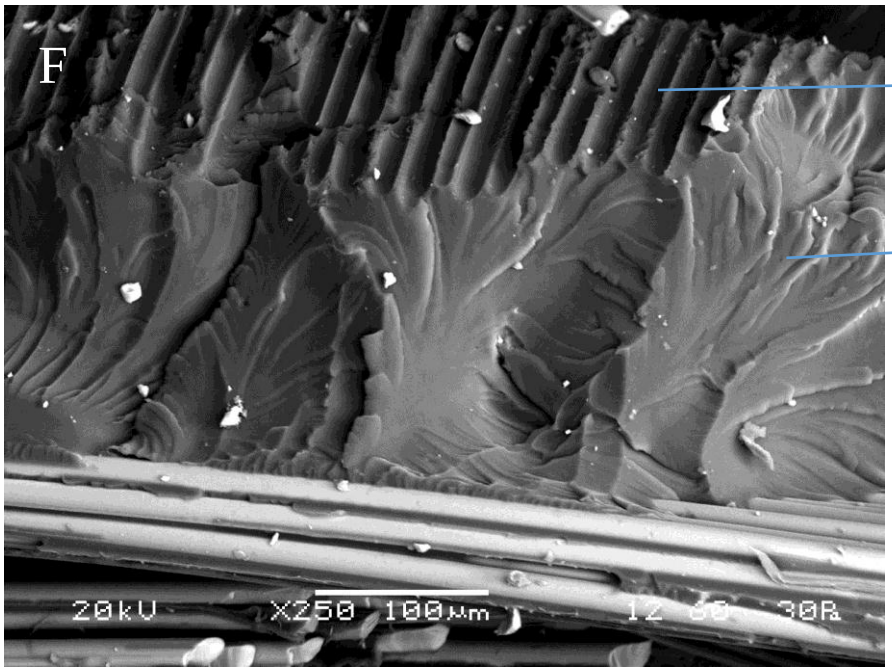


Multi Walled Carbon Nano-Tube


C
Fibre Breakage
River-line Markings
Fragmented Fibre
20kV X350 50µm 13 60 30R


D
Degraded Matrix
Pit
River-line markings
20kV X500 50µm 13 60 30R


E
Brittle Fracture
Fibre Imprint
20kU X500 50µm 12 60


F
Fibre Imprint
River-line Markings
20kU X250 100µm

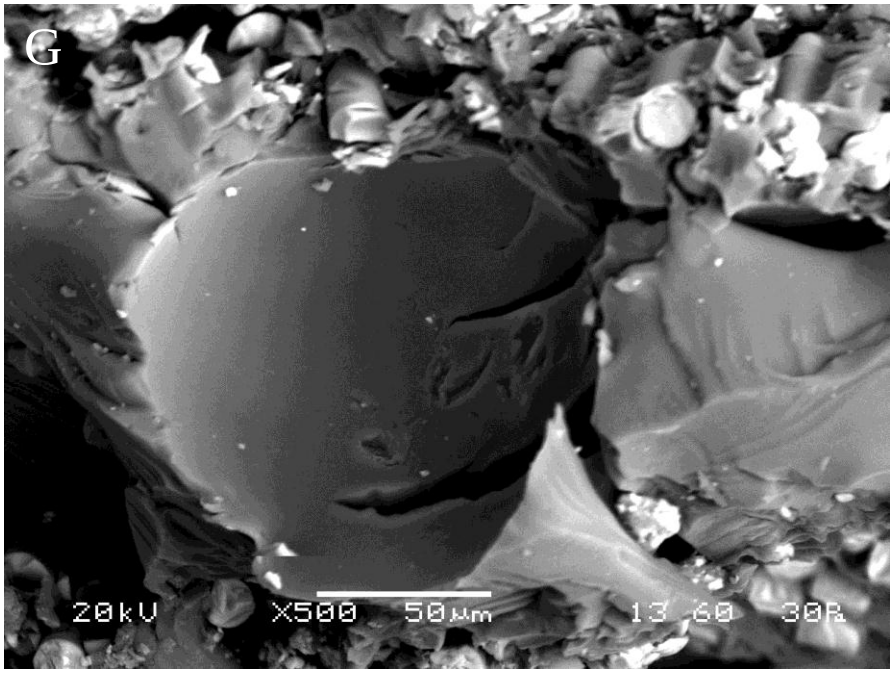
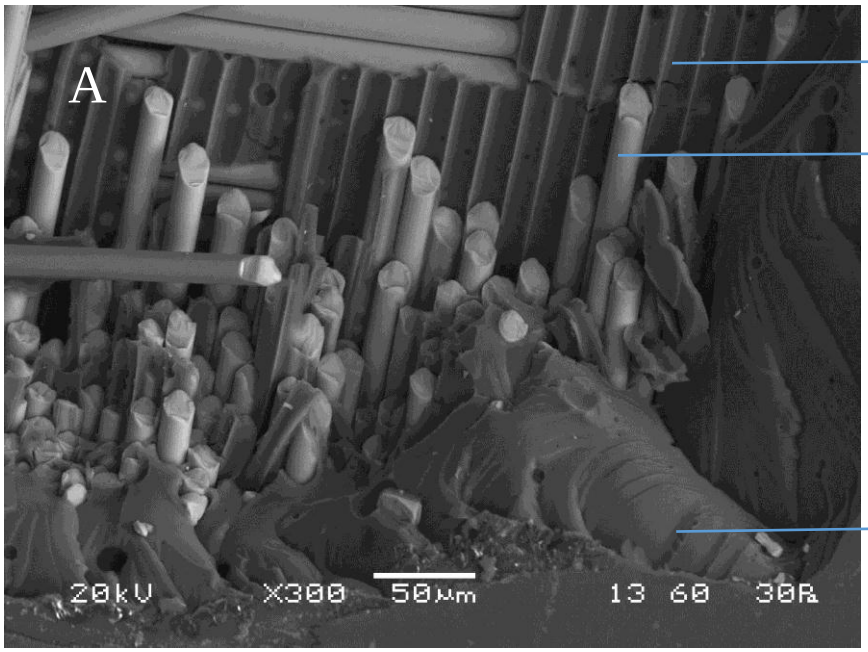


Fig 29: Scanning Electron Micrograph of fractured FRP composite without conditioning (A) 0% CNT (B) FESEM 0.1% CNT(C) 0.1% CNT (D) 0.3% CNT (E) 0.3% CNT (F) 0.5% CNT (G) 0.5% CNT

Fig. 29: shows various modes of failure in GFRP composite. (B) is a FESEM image which shows uniform dispersion of CNT. This homogeneous distribution is responsible for high mechanical properties shown by 0.1% CNT, this increases the interfacial area and hence good load transfer from matrix to fibres.

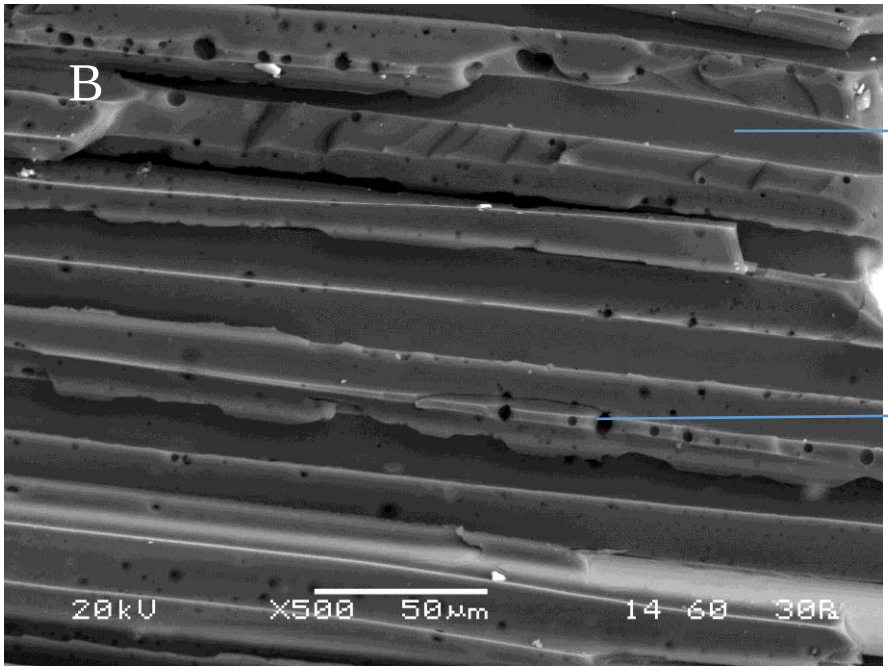
4.4.2) Room Temperature Water (35˚C)



Delamination

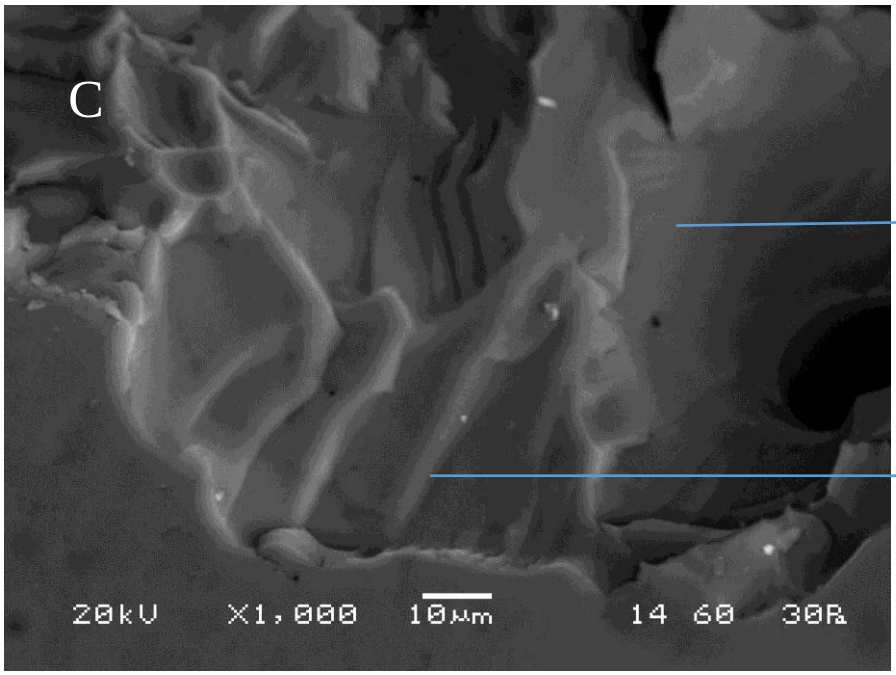
Fibre Breakage

River-line Markings



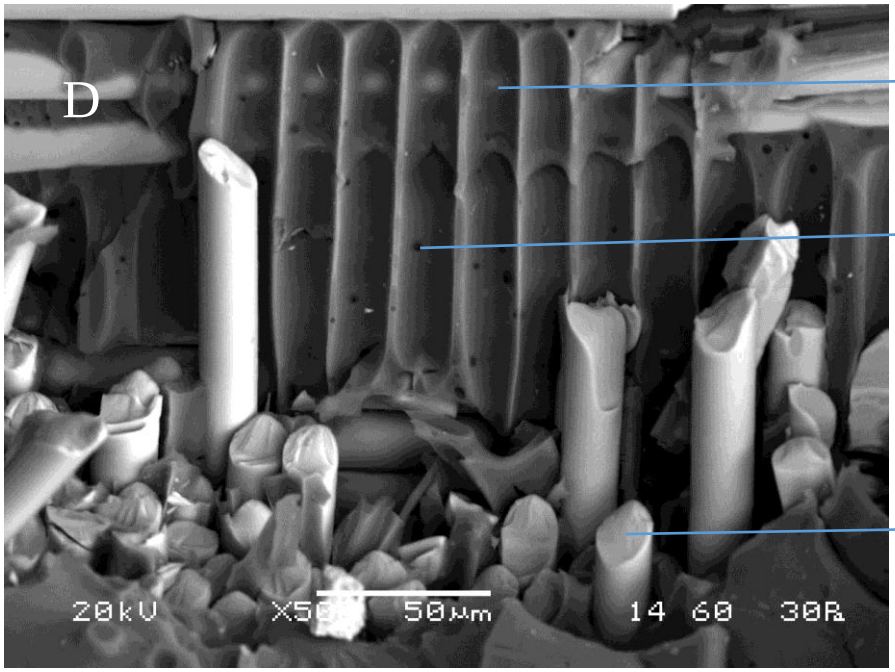
Fibre Imprints

Voids



Matrix Degradation

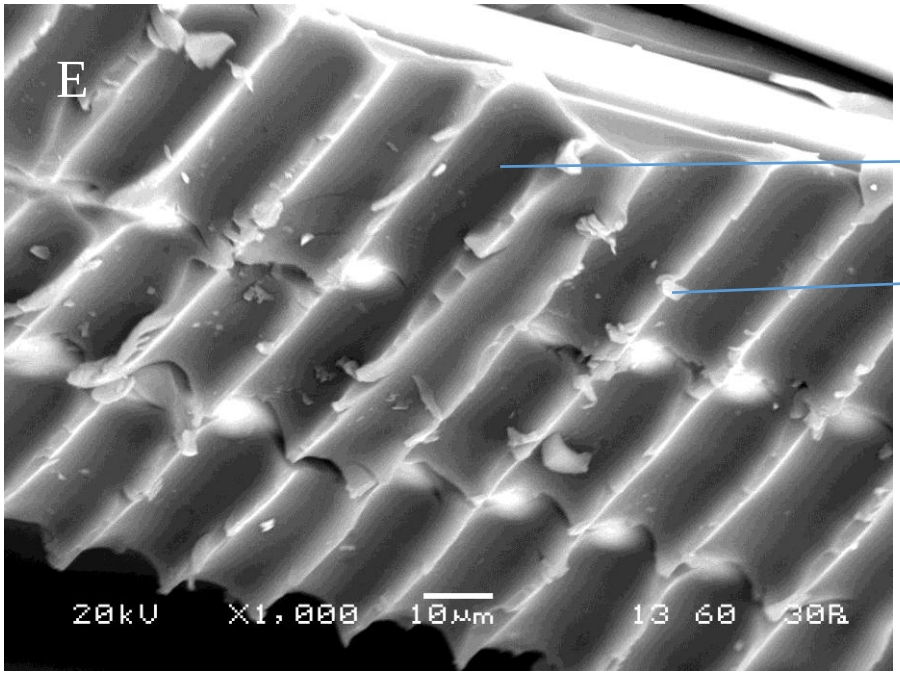
River-line Markings

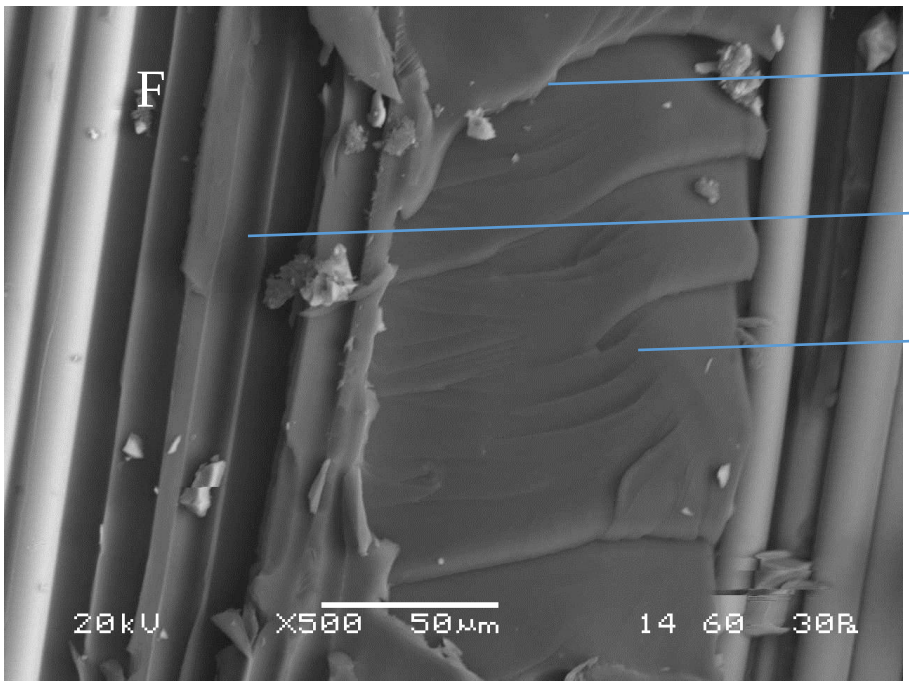


Fibre Imprints

Voids

Fibre Breakage


E
Fibre Imprints
Platinum Sputter
20kV X1,000 10µm 13 60 30R


F
Matrix Degradation
Fibre Imprints
River-line Markings
20kV X500 50µm 14 60 30R

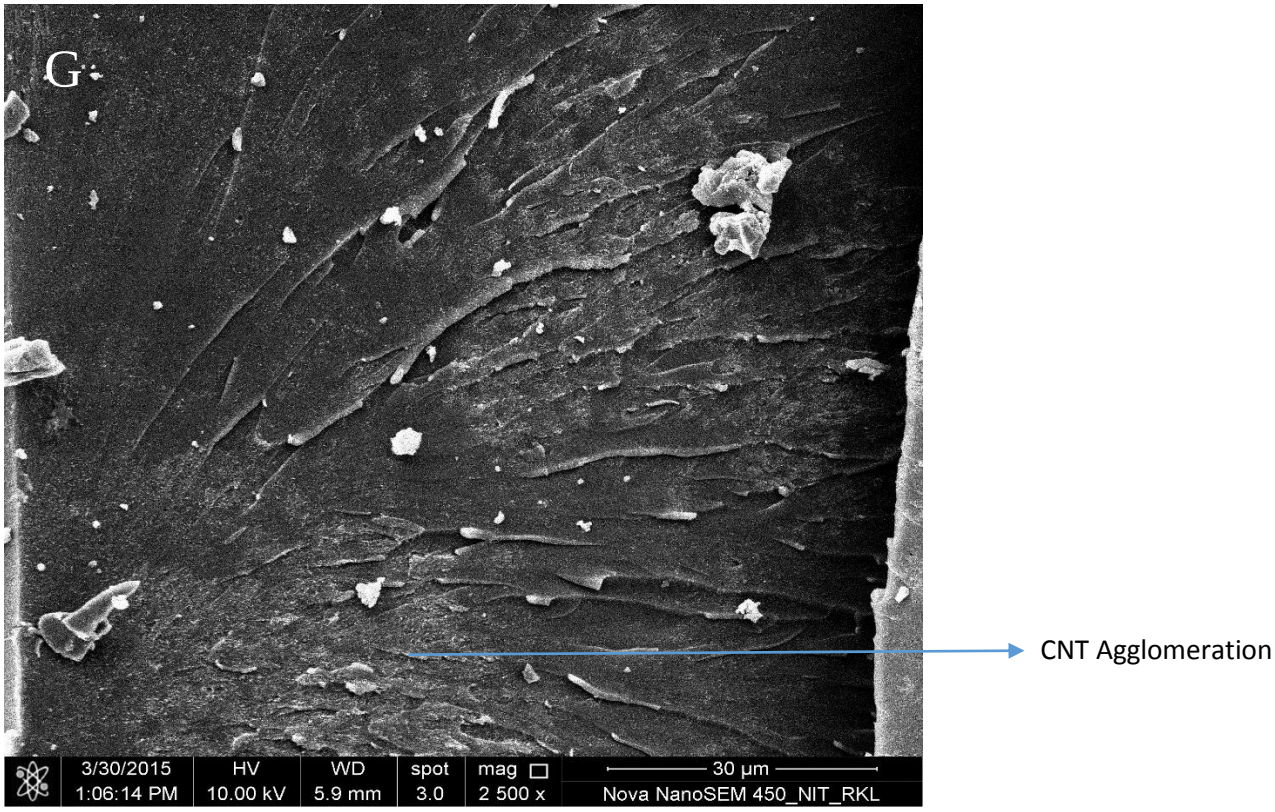
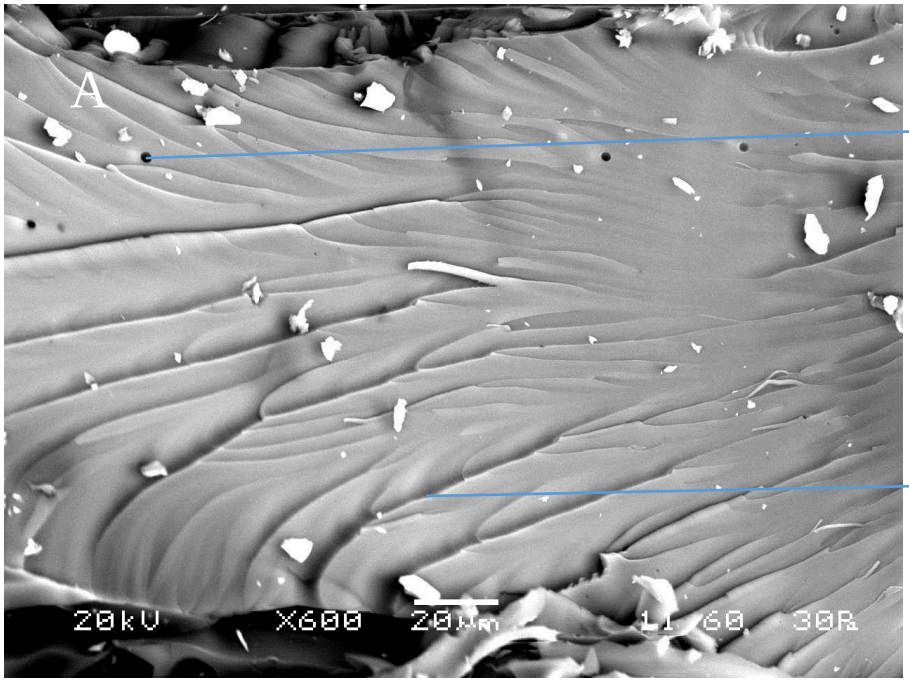


Fig. 30: Scanning Electron Micrograph of fractured FRP composite when conditioned for 410 Hours in 35˚C water with (A) 0% CNT (B) 0% CNT (C) 0.1% CNT (D) 0.1% CNT (E) 0.3% CNT (F) 0.5% CNT (G) FESEM 0.5% CNT

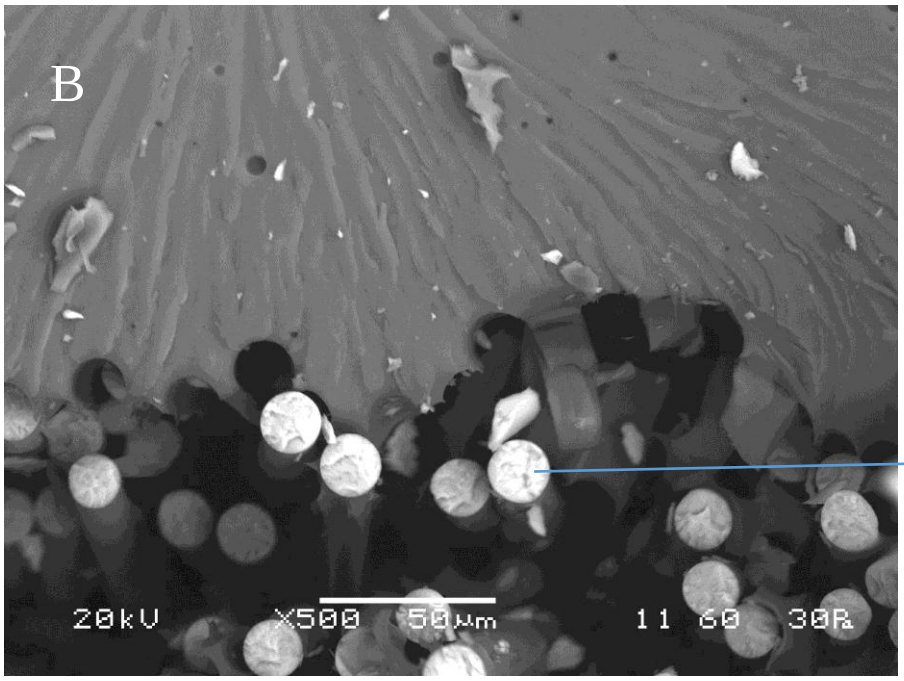
Fig. 30: (G) shows agglomeration of CNT at higher weight percentage of CNTs due to non-uniform dispersion of CNTs in the matrix. This is more prevalent in 0.5% CNT, which shows inferior properties as compared to other lower weight percentage of CNTs.

4.4.3) Cold Water (5˚C)

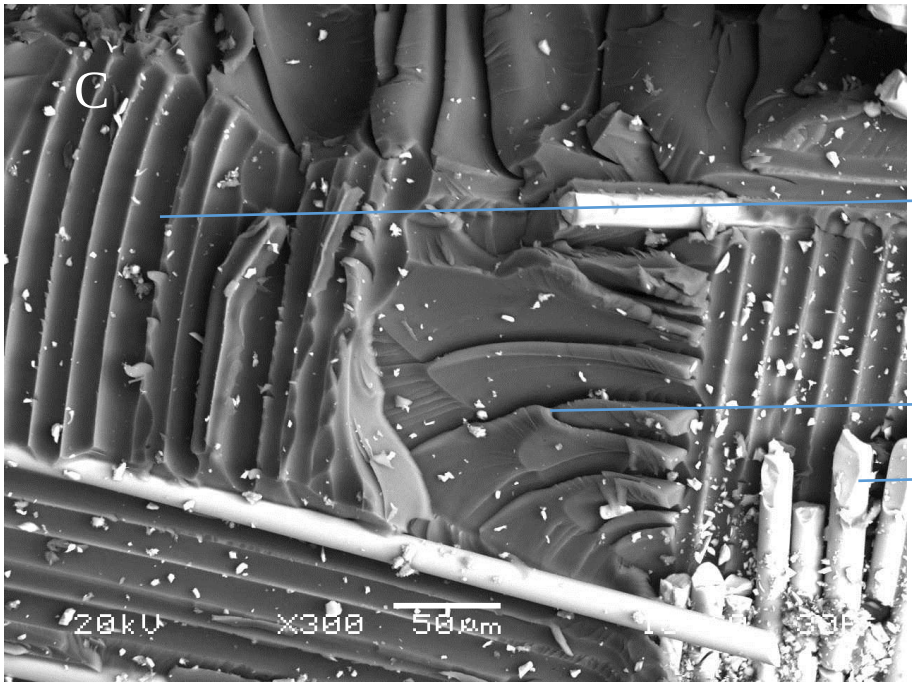


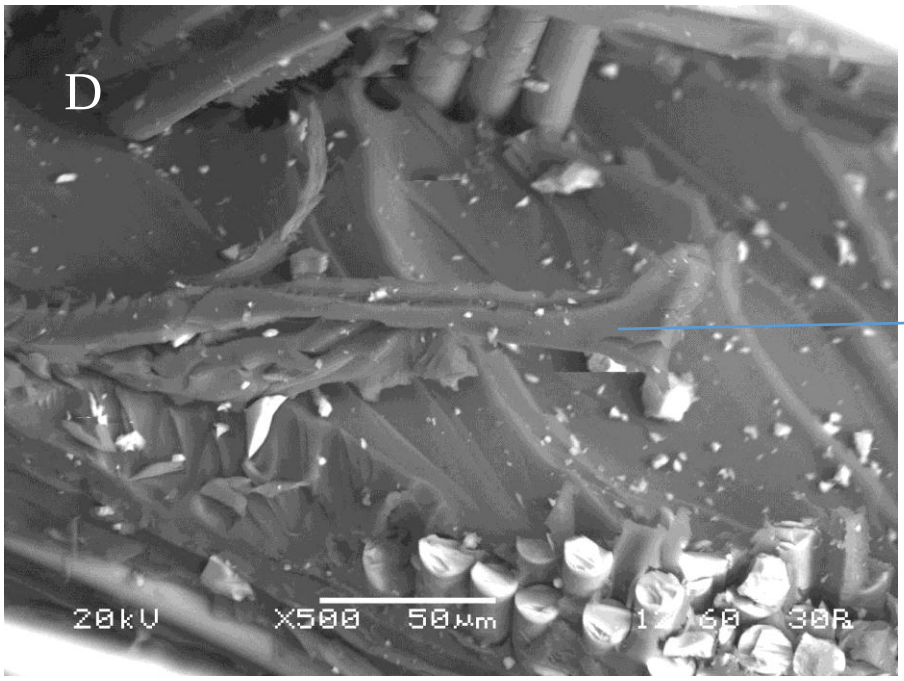
Void

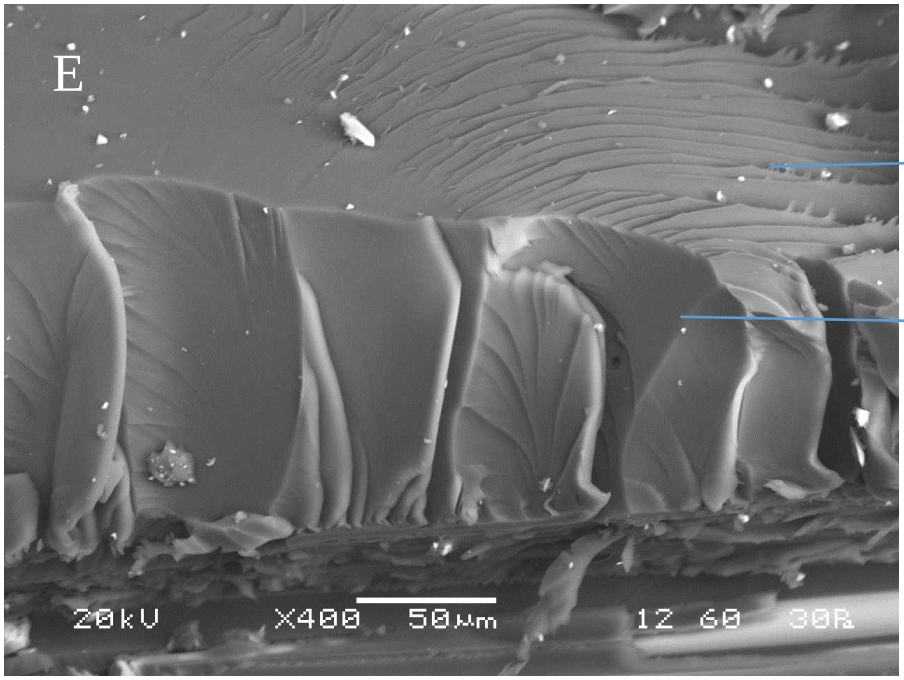
River-line Markings



Brittle Fracture

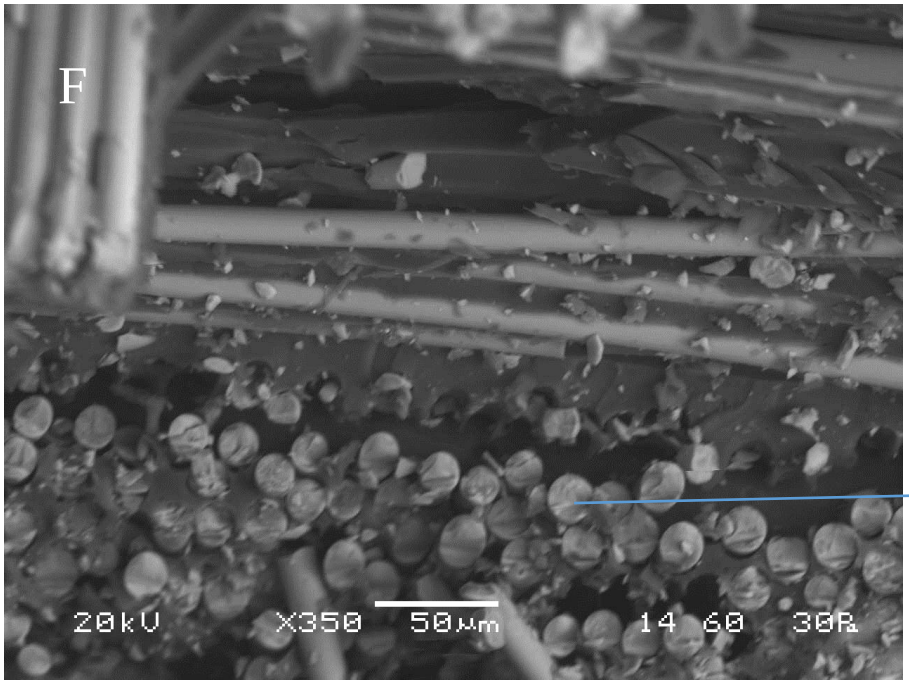

C
20kV X300 50µm
Fibre Imprint
River-line Markings
Fibre Breakage


D
20kV X500 50µm
Matrix Degradation



River-line Markings

Shear Cusps



Brittle Fracture

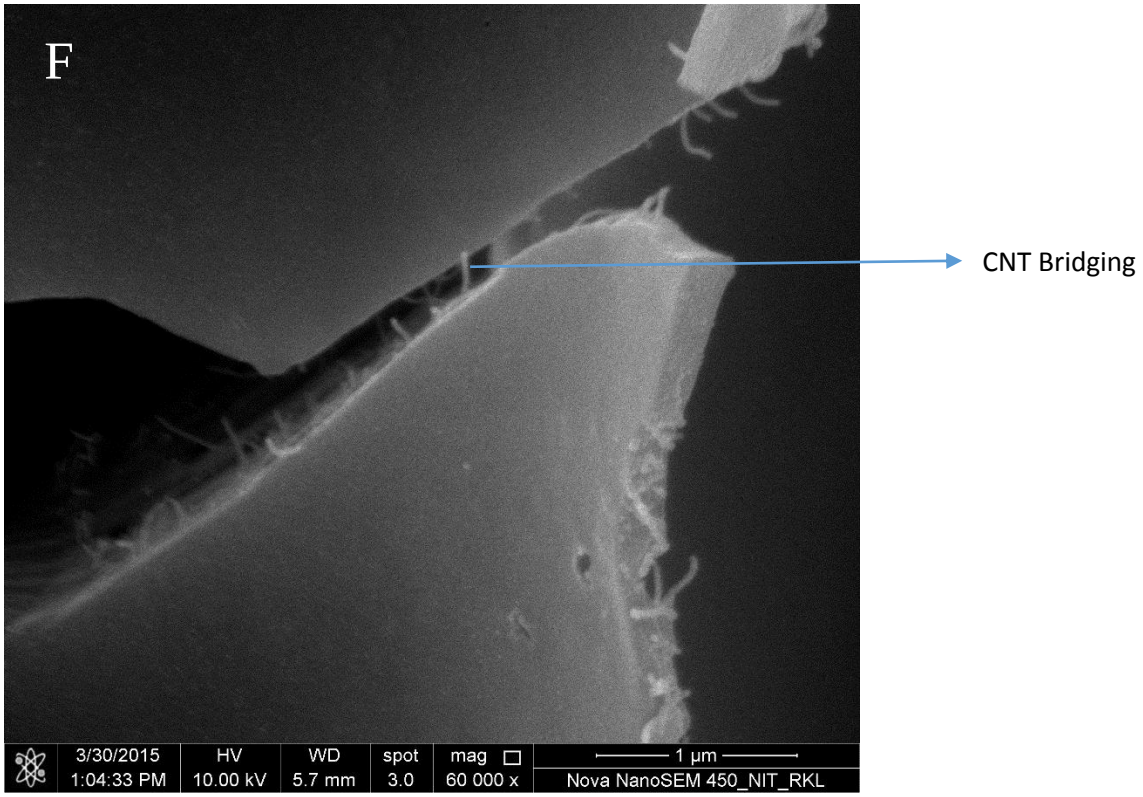


Fig. 31: Scanning Electron Micrograph of fractured FRP composite when conditioned for 186 Hours in 5˚C water with (A) 0% CNT (B) 0% CNT (C) 0.1% CNT (D) 0.3% CNT (E) 0.3% CNT (F) 0.5% CNT (G) 0.1% CNT

In fig. 31: (G) is a FESEM image which shows an important aspect of using CNT i.e. CNT bridging. CNT bridges the crack between the matrix and hence prevents failure to a certain limit.

\

5) CONCLUSION:

5.1) Room temperature Water (35°C)

Moisture ingression behaviour in different material systems were studied which showed GFRP+0.1% CNT absorbed least amount of moisture and had the least amount of diffusivity. This was due to uniform dispersion of CNTs in the polymer matrix which increased the interfacial surface area, and hence, better load transfer from matrix to fibre. This results in better properties as compared to its counter parts. But, a degradation in properties were observed in all the material system with increasing exposure to room temperature water (35°C).

5.2) Cold Water (5°C)

Moisture ingression behaviour in different material systems were studied which showed GFRP+0.1% CNT absorbed least amount of moisture and had the least amount of diffusivity. This results in better properties as compared to its counter parts. After some exposure to cold water, an increase in the mechanical properties were observed due to matrix hardening for all material systems. But, after long exposure there might be some deleterious effect on mechanical properties.

5.3) Hygrothermal Conditioning

Mechanical behaviour of moisture ingressed samples at different loading rates were studied, which showed that better mechanical properties were observed at 100mm/min due to higher energy requirement for failure. On studying moisture ingression kinetics it was observed that ILSS samples absorbed moisture at a faster rate as compared to flexural samples due to its high surface to volume ratio.

5.4) Effect on the failure modes of FRP Composites

On studying the SEM fractographs the various failure modes in the FRP composites were revealed. After moisture ingression, nucleation of microcracks occurs due to plasticisation and swelling. This also leads to matrix degradation and cracking. The fractured glass fibre surfaces show evidence brittle failure. CNT agglomeration is observed in high CNT concentration composites responsible for degradation in properties. Properly dispersed CNTs are helpful in CNT bridging which reduce the rate of propagation of cracks.

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